Correlated ground state ab initio studies of polymers

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vorgelegt von

Ayjamal Abdurahman

aus

Xinjiang

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1. Introduction

Polymers are well-known materials from every day life, and are, moreover, also important for certain applications in advanced technologies and are found in many biological systems [1]. Therefore, the investigation of polymers is one of the fastest developing fields of today's material science. In addition to the large variety of experimental methods, the theoretical description of polymers becomes more and more important. Recent progress in this field depends on the development and improvement of the methodology and also the rapid progress of modern high–performance computers.

In this thesis we have studied correlated ground state properties of polymers by employing wave-function-based quantum chemical *ab initio* techniques. In the first part of the thesis we briefly summarized the Hartree-Fock and correlation methods for atoms and molecules. In the second part we described the extension of these methods to solids and polymers. In the third part we presented the application of these methods to polymers. Currently, two approximate schemes are used extensively for performing *ab initio* calculations on the full electronic Hamiltonian. [The word *ab initio* does not mean that one has an exact solution of the electronic Schrödinger equation, but it does mean that in the fixed-nuclei (Born-Oppenheimer) approximation one takes into account all electrons of the system and treats all interactions explicitly.] One is the Hartree-Fock (HF) approximation. Another one is density-functional theory (DFT), which is usually treated in the so-called local density approximation (LDA). Both approximations are effective single-particle theories.

Hartree-Fock (HF) is a mean field theory, in which each electron has its own wavefunction (orbital), which in turn obeys an effective one-electron Schrödinger equation. The effective Hamiltonian (Fock operator) contains the avarage field (Coulomb and exchange) of all other electrons in the system. The total electronic wave function is the antisymmetrized product of the orbitals—Slater determinant (SD). However, the HF approach serves as an essentially zeroth-order approximation to the ground state of interacting electrons. By construction, the HF equations are a well-defined approximation to the Schrödinger equation and constitute the starting point for a variety of subsequent treatments. It is in this sense that any effects beyond HF are usually referred to as correlation effects, namely the HF total energy differs from the exact non-relativistic energy by an energy, which for historical reasons is called the correlation energy.

The another most widely used approach in polymers or solids is density functional theory (DFT). The DFT for an electronic system is based on the theorem [2] which states that

the ground-state energy is a unique functional of the electron density. The minimum value of the total-energy functional is the ground-state energy, and the density giving this minimum is the exact single-particle ground-state density. Kohn and Sham [3] showed how it is formally possible to replace the many-electron problem by an equivalent set of self-consistent one-electron equations. These equations have the same form as the HF equations, except that they contain a more general local potential [4]. In principle the method leads to a tremendous simplification to the many electron problem since the electronic density is significantly less complex than the many-electron wave function. However, in contrast to wave-function-based formalisms of quantum mechanics, the relationship between the ground state energy and the electronic density is not obvious and the development of the computational formalism was dependent on first obtaining good approximations to the energy functional. The simplest but very successful one is the local-density approximation (LDA), in which the unknown functional of density is approximated by a spatial integral over a given function of the local density, modelled on the behaviour of the free electron gas. A number of different parameterizations proposed to the LDA is summarized in the reference [5]. Nevertheless, in this method one avoids constructing the many-body wave function of the system and instead computes directly ground-state properties such as the total energy, lattice constant, etc., from its charge density. On the other hand, some correlation effects, which by definition are not included in HF, are also taken into account in this method, albeit not in a controlled or systematic way.

To be able to calculate accurately different properties of polymers it is usually necessary to include the effects of electron correlations into the theory. It is well known that electron correlations plays a key role in understanding the most interesting phenomena in molecules and solids [6]. It has been the focal point for many years in atomic and molecular electronic structure theory [7] and various correlated methods have been developed [8]. Among them are many-body perturbation theory [9] and its infinite-order generalization, coupled-cluster (CC) theory [10, 11], which provides a systematic way to obtain the essential effects of electron correlation. We will futher discuss them in chapter 2. As in finite systems, electron correlation is critical to a description of many of the most interesting problems in extended systems such as polymers [12]. Although it remains one of the most difficult problems in the field of the electronic structure theory, some significant progress has recently been made in the theory and their application. An initial step towards an *ab initio* treatment of electron correlation in infinite systems is the formulation and coding of a Hartree–Fock method. The HF method based on the use of Bloch orbitals is well developed for polymers in its *ab initio* form. The state of the art in these approaches is represented by the CRYSTAL program which expands the Bloch orbitals in terms of Gaussian-type functions (GTFs) and obtains the canonical SCF solutions. However, the Bloch functions are completely delocalized in character, and thus by themselves are not a good starting point for a subsequent *ab initio* treatment of electron correlations. The electron correlation effects are mostly local, therefore, localized orbitals provide a better starting point for an *ab initio* treatment of electron

correlations. In the localized representation one can describe the correlation by means of a finite number of virtual excitations of the HF state in which one of the electrons involved will be in the reference cell and other ones could be in the reference cell or in a unit cell close by. In principle one could always transform the Bloch orbitals to a localized representation using a suitable localization procedure, e.g., the Foster-Boys localization scheme [13], in practice achieving a good localization appears to be quite difficult.

During the last years, the HF approach was developed in our group which allows the direct determination of (localized) Wannier-type orbitals of an infinite solid. Physically it employs an "embedded-cluster" picture of a crystalline solid. The main philosophy behind the embedded-cluster approach as applied to a perfect solid is that a solid can be seen as a central unit cell (called the "central cluster") embedded in the field created by the rest of the unit cells (called the "environment") which are identical to the central unit cell except for the fact that they are spatially separated from it by multiples of the unit vectors of the crystal. Thus one solves the HF equations of this embedded cluster to obtain Wannier-type functions of the electrons of the unit cell. These Wannier-type orbitals in turn are used to construct the orbitals of the rest of the solid, and the procedure is iterated until self-consistency is achieved. The localization of orbitals is achieved self-consistently by means of environment projection operators. The method and its computer implementation will be discussed in detail in chapter 3. The correlations will be included by considering local virtual exitations from the reference wave function, keeping the rest of the infinite solid frozen at the HF level. The computational scheme to be used for this will be the "incremental method" of Stoll [14, 15, 16]. The basic idea is, that the HF energy is obtained from Bloch orbital [17, 18] or Wannier orbital [19] calculations and the correlation energy in basis of Wannier orbital expanded in sum over one-, two-, ... body/group contributions. Another method alternative to the incremental scheme is the so-called simplified approach, in which the correlation energy per unit cell is obtained from the correlation energy difference of two oligomers differing by one unit cell. The incremental scheme and a simplified finite cluster approach will be discussed in detail in section 3.2.

In this thesis the correlation energy is calculated by applying standard quantum-chemical methods such as the configuration interaction (CI) method, Møller–Plesset second–order perturbation theory (MP2), and the coupled–cluster ansatz (CC). In all approaches electron correlation effects are introduced by admixing to the HF determinant additional determinants which are generated by replacing occupied spin orbitals in the HF wave function by unoccupied spin orbitals, and may be classified as single, double, triple, quadruple, etc. excitations, involving unknown expansion coefficients.

The conceptually most simple approach is the traditional CI method, where the unknown expansion coefficients are determined variationally. If all possible excitations are included, the method gives the exact solution within the given basis set, and is referred to as full configuration interaction (FCI). Although, FCI is the straightforward and general approach for the treatment of electron correlation using realistic one-particle basis

sets, it is only feasible for small systems with at most ten electrons. The number of determinants and configuration state functions in FCI goes up factorially with the basis set size. Therefore in most applications it is necessary to truncate the CI expansion space in some way to make the calculation feasible. However, the principal weakness of truncated CI is its lack of proper scaling with the size of the system. The proper scaling of a computational model, referred to as 'extensivity' or 'size-extensivity', is the main facet of the 'separability condition' $E(nX) = nE(X)$, for n identical subsystems X. Since the size of a periodic polymer is infinite, size-extensivity is an essential prerequisite for a correlated theory to be applied to extended systems. It is well known that many-body perturbation theory (MBPT) and coupled-cluster (CC) theory have this property, and so they are appropriate tools for extended systems. The simplest correlated method is second-order MBPT that treats the electron correlation as a perturbation on the HF problem, e.g., MP2. It is easily shown that the HF energy is correct to first order, thus perturbation energies start contributing from second order. For MP2 the explicit expressions have been presented and implemented for infinite, periodic one-dimensional polymers [20, 21].

The electron correlation techniques which are receiving most attention recently are coupled-cluster (CC) methods. The exponential form of the excitation operator used in CC theory is an effective way of including the effects of higher excitations and also ensures size-extensivity. Recently, CC methods for polymers have been pursued by Förner, Ladik and coworkers [22]. They drived the equations with localized orbitals and applied the coupled-cluster doubles (CCD) and its linear approximation (L-CCD) to compute total energy per unit cell in different polymers. Since it is much more difficult to implement and requires more computational effort than MBPT, the method was executed with futher approximations which prohibit an accurate assessment of the method. In this thesis, because of the availability of quantum chemical programs such as MOLPRO [23] with efficient implementations of correlation approaches, we have evaluated the electron correlations mainly from finite cluster calculations using the simplified approach by applying MP2 and coupled-cluster theory with singles and doubles (CCSD), including a perturbative estimate of triples (CCSD(T)). The application of the standard correlated quantum chemical methods such as FCI, MP2, CCSD, and CCSD(T) to polymers are presented in chapter 4. The MP2, CCSD, and CCSD(T) methods are applied to the polymers polyaminoborane, polyiminoborane, polycarbonitrile, and beryllium hydride. The model system lithium hydride chain was studied using a combination of the FCI method and the incremental scheme where the Wannier-type orbitals have been directly taken from the corresponding HF calculation of the infinite system instead of from finite cluster calculations. We have optimized structural parameters and calculated cohesive energies as well as polymerization energies. For polyaminoborane and polyiminoborane we have also presented the band structure at the HF and MP2 level. The results presented here led to three publications [24, 25, 26].

2. Overview of Quantum Chemical Methods for Atoms and Molecules

2.1. The Hartree-Fock Method

In quantum chemistry we are mostly interested in solving the Schrödinger equation assuming that the exact solution would lead to a complete description of the system. The physical state of the system is fully described by a state function which depends on the spatial and spin coordinates of all particles in the system. For stationary states the electronic wave-function can be obtained by solving the time-independent Schrödinger equation:

$$H\Psi(1,...N) = E\Psi(1,...N) \tag{2.1}$$

where H is the electronic Hamiltonian describing the motion and interaction of N-electrons and E and Ψ are the total energy and N-electron wave function of the system, respectively. The nonrelativistic N-electron Hamiltonian in the so-called Born-Oppenheimer approximation (in which the electrons are considered as moving in the field of fixed nuclei) usually can be written as (in atomic units):

$$\hat{H} = \sum_i \hat{h}_i + \sum_{i<j} \hat{g}_{ij} + \hat{h}_0 \tag{2.2}$$

where $\hat{h}_i$ is the one-electron term

$$\hat{h}_i = -\frac{1}{2}\nabla_i^2 - \sum_A \frac{Z_A}{r_{iA}} \tag{2.3}$$

describing the kinetic energy and the nucleus-electron Coulomb attraction for the i-th electron. The $\hat{g}_{ij}$ is a two-electron operator

$$\hat{g}_{ij} = \frac{1}{r_{ij}} \tag{2.4}$$

and describes the Coulomb repulsion between the electrons i and j. The last term

$$\hat{h}_0 = \sum_{A<B} \frac{Z_A Z_B}{|R_A - R_B|} = \sum_{A<B} \frac{Z_A Z_B}{R_{AB}} \tag{2.5}$$

describes the nucleus-nucleus Coulomb repulsion and implies n additive constant for fixed nuclear positions, which we will usually leave outside the discussion in the rest of this chapter. Here again we recall that the indices i and j label the electrons, A and B the nuclei.

The Schrödinger equation for a many-electron system cannot be solved exactly due to the electron-electron repulsion and therefore approximations are required. The most popular approximations are based on the Hartree-Fock (HF) method. In this context, the N-electron Schrödinger equation is replaced by a set of effective one-electron equations (Fock equations) which have the orbitals as eigenfunctions. The N-electron wavefunction $\Psi^{HF}(1,...N)$ is then constructed as an antisymmetrized product of the occupied molecular orbitals:

$$\Psi^{HF}(1,...N) = (1/\sqrt{N!})\hat{A}|\chi_1(1).....\chi_N(N)| \tag{2.6}$$

where $\hat{A} = \sum_p (-1)^p \hat{p}$, $\hat{p}$ is a permutation operator, $(-1)^p$ is $+1$ or -1 for even and odd permutations, respectively. $\chi_i(i)$ denotes a molecular spin orbital (MSO) (which includes both its spatial and spin parts) and represents a one-electron wavefunction. Without loss of generality the molecular spin orbitals $\chi_i(i)$ usually can be assumed to be orthogonal to each other. Such a wavefunction is called a single-determinant (Slater determinant) wavefunction. In building up a determinantal wavefunction, the usual practice is to choose a set of molecular orbitals, and then to assign electrons of α (spin up) or β (spin down) spin to these orbitals. It is not possible for a molecular orbital to be occupied by two electrons of the same spin. This is the *Pauli exclusion principle*, which follows because the determinantal wavefunction equation (2.6) vanishes if two columns (or rows) are identical. Therefore orbitals may be classified as doubly occupied, single occupied or empty. Many molecules have an even number of electrons in their ground (lowest energy) states and may be represented by *closed-shell wave functions* with orbitals either doubly occupied or empty. The discussion in the remainder of this chapter will be restricted to the closed-shell case.

Now the question is: How can we find the best approximate ground state wavefunction of the Hamiltonian? According to the variational principle,

$$E_{0,exact} \leq E_{0,approximate} = \frac{<\Psi|\hat{H}|\Psi>}{<\Psi|\Psi>} \tag{2.7}$$

the "best" MSOs are those which minimize the electronic ground state energy E_0

$$\begin{aligned} E_{HF} &= \sum_i <\chi_i|\hat{h}|\chi_i> + \frac{1}{2}\sum_{ij}(<\chi_i\chi_j|\hat{g}|\chi_i\chi_j> - <\chi_i\chi_j|\hat{g}|\chi_j\chi_i>) \\ &= \sum_i h_{ii} + \frac{1}{2}\sum_{ij} <ij||ij> \end{aligned} \tag{2.8}$$

Using the method of Lagrange multipliers, we can systematically vary the form of the MSO χ_i subject to maintaining their orthogonality $<\chi_i|\chi_j> = \delta_{ij}$ until the energy E

is a minimum, then we get the following Hartree-Fock integro-differential equations:

$$\hat{F}|\chi_i >= \sum_j \Lambda_{ij}|\chi_i > . \tag{2.9}$$

By a unitary transformation we can obtain the set of canonical orbitals

$$\hat{F}|\chi_i >= \varepsilon_i|\chi_i > \tag{2.10}$$

where $\hat{F}$ is the Fock operator

$$\hat{F} = \hat{h} + \hat{J} - \hat{K}. \tag{2.11}$$

The eigenvalues ε_i are obtained from the diagonal form of the Fock matrix. The Coulomb operator

$$\hat{J} = \sum_j \hat{J}_j$$

with

$$\hat{J}_j(\mathbf{r})\chi_i(\mathbf{r}) = \left[\int d\mathbf{r}'\chi_j{}^*(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\chi_j(\mathbf{r}')\right]\chi_i(\mathbf{r}) \tag{2.12}$$

and the exchange operator

$$\hat{K} = \sum_j \hat{K}_j$$

with

$$\hat{K}_j(\mathbf{r})\chi_i(\mathbf{r}) = \left[\int d\mathbf{r}'\chi_j{}^*(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\chi_i(\mathbf{r}')\right]\chi_j(\mathbf{r}) \tag{2.13}$$

are most easily defined via their action on a particular orbital χ_i. Equation (2.10) can be interpreted as a set of effective one-electron Schrödinger equations for the orbitals. They are often referred to as the *canonical Hartree-Fock equations*. The corresponding orbitals are the canonical HF orbitals, and the eigenvalues are referred to as orbital energies and are given by $\varepsilon_i =< \chi_i|\hat{F}|\chi_i >$. If we add up the orbital energies we get

$$\sum_i \varepsilon_i = \sum_i h_{ii} + \sum_{ij} < ij||ij > \tag{2.14}$$

If we compare this with equation (2.8), we find the total energy is not simply the sum over the orbital energies but, instead, given by

$$E = \sum_i \varepsilon_i - \frac{1}{2}\sum_i < \chi_i|\hat{J} - \hat{K}|\chi_i >= \frac{1}{2}\sum_i(\varepsilon_i + h_{ii}) \tag{2.15}$$

So far we considered the HF equations from a formal point of view in terms of a general set of MSOs. In the actual calculation of the HF wave functions, we must be more specific about the form of the MSOs. Usually, we have two types of MSOs: restricted MSOs, which are constrained to have the same spatial function for α and β spin functions; and unrestricted MSOs, which have different spatial functions for α and β spins. In this thesis we consider only the spin-restricted HF formalism.

2.1.1. The Roothaan-Hall Method

Even though the HF approximation represents an immense simplification compared to the original Schrödinger equation, the resulting equations are still too complicated to be solved exactly for most systems of chemical interest. Therefore, in practice the HF equation is solved by expressing the spatial part φ_i of a MSO χ_i as a linear combination of atomic orbitals (MO-LCAO approximation)

$$\varphi_i(r) = \sum_{p=1}^{n} C_{pi}\phi_p(r) \qquad\qquad i = 1, 2, ..., N \tag{2.16}$$

in which each AO can be described by one or more so called basis functions. The larger the number of basis functions, the closer the result of the calculation comes to the HF numerical limit. These basis functions are usually centered at different atoms and appropriate choices will be discussed in next section. From equation (2.16), the problem of calculating the HF molecular orbitals reduces to the problem of calculating the set of expansion coefficients C_{pi}. We can obtain a matrix equation for the C_{pi} by substituting the linear expansion into the HF equation (2.10). They were derived for the closed-shell structure by Roothaan [27] and Hall [28]. The *Roothaan-Hall equations* are

$$\sum_{q=1}^{n}(F_{pq} - \varepsilon_i S_{pq})C_{qi} = 0 \tag{2.17}$$

with the normalization conditions

$$\sum_{p=1}^{n}\sum_{q=1}^{n} C_{pi}^{*} S_{pq} C_{qi} = 1 \tag{2.18}$$

Here, ε_i is the *one-electron energy* of molecular orbital φ_i, S_{pq} is the *overlap matrix* element

$$S_{pq} = \int dr_1 \phi_p^{*}(1)\phi_q(1) \tag{2.19}$$

and F_{pq} is the *Fock matrix* element

$$F_{pq} = H_{pq}^{core} + \sum_{r=1}^{n}\sum_{s=1}^{n} P_{rs}[(pq|rs) - \frac{1}{2}(pr|qs)] \tag{2.20}$$

In this expression, H_{pq}^{core} is a matrix representing the energy of a single electron in a field of "bare" nuclei. Its elements are

$$H_{pq}^{core} = \int dr_1 \phi_p^{*}(1) h(1) \phi_q(1) \tag{2.21}$$

The quantities $(pq|rs)$ appearing in equation (2.20) are *two-electron repulsion integrals*:

$$(pq|rs) = \int\int dr_1 dr_2 \phi_p^{*}(1)\phi_q(1) r_{12}^{-1} \phi_r^{*}(2)\phi_s(2) \tag{2.22}$$

They are multiplied by the elements of the one-electron *density matrix*, P_{rs},

$$P_{rs} = 2\sum_{i=1}^{occ} C_{ri}^{*} C_{si} \tag{2.23}$$

The summation is over *occupied* molecular orbitals only. The factor of two indicates that *two electrons* occupy each molecular orbital.
The electronic energy is now given by

$$E = \frac{1}{2}\sum_{p=1}^{n}\sum_{q=1}^{n} P_{pq}(F_{pq} + H_{pq}^{core}) \tag{2.24}$$

which, when added to equation (2.5), yields an expression for the total energy.
The Roothaan-Hall equation (2.17) are only formally linear since the Fock matrix F_{pq} itself depends on the molecular orbital coefficients C_{pi}, through the density matrix expression (2.23). Therefore their solution necessarily involves an iterative process. Since the resulting molecular orbitals are derived from their own effective potential, the technique is frequently called *self-consistent-field (SCF)* approach.

2.1.2. Basis Functions and Basis Sets

As described in the previous section, in practical applications of the theory, a further restriction is imposed, requiring that the individual molecular orbitals be expressed as linear combinations of a finite set of n prescribed one-electron functions known as *basis functions*. Currently, two types of atomic basis functions have received widespread use. One is *Slater-type atomic orbitals (STOs)* given as

$$\phi_{n,l,m} = N(\mathbf{r} - \mathbf{R})^{(n-1)} exp[-\zeta(\mathbf{r} - \mathbf{R})] Y_{l,m}(\theta, \phi) \tag{2.25}$$

Here N is a normalizing constant, n denotes a principal quantum number and ζ is an arbitrary positive number called the orbital exponent. STOs provide reasonable representations of atomic orbitals with standard ζ-values. However, in the presence of more than two atoms, the integral evaluation over STOs basis functions is very time consuming. This has lead to an alternative choice of basis functions.
The second type of basis consists of *Cartesian Gaussian-type basis functions* (CGTFs) which were introduced by Boys [29] and given as the following form:

$$\phi_{\mathbf{r},\zeta,\mathbf{n},\mathbf{R}} = N(x - R_x)^{n_x}(y - R_y)^{n_y}(z - R_z)^{n_z} exp[-\zeta_p(\mathbf{r} - \mathbf{R})^2] \tag{2.26}$$

where N is still a normalizing constant, $\mathbf{n} = (n_x, n_y, n_z,)$. ζ_p denotes the orbital exponent and the vector $\mathbf{R}$ represents the center of the basis function. The centers of the basis functions $\mathbf{R}$ are normally taken to be at the locations of the appropriate atoms of the system. CGTFs with $n_x + n_y + n_z = 0, 1, 2, ...$ are (in a loose sence) called, respectively, $s, p, d, ...$ type basis functions. The individual basis functions of the form

of equation (2.26) are called *primitive* functions while the linear combinations of them are called the *contracted* functions. However, the advantage of using CGTFs is that the evaluation of the three- and four-center electron repulsion integrals reduces to two-center integrals since the product of two Gaussian functions on two different centers is a Gaussian function centered at a point somewhere between the two. Currently almost all *ab initio* calculations are carried out with a basis set of contracted Gaussians. The advantage is that it reduces the number of basis functions quite significantly and gives large savings in computational time.
Quantum chemical methods, whether HF, CI, MBPT, or CC and also KS-DFT begin the calculation with the choice of a basis set, i.e., a set of basis functions. The use of an adequate basis set is an essential requirement for the success of the calculation and it is classified as following:
—A minimal basis set: it has a single basis function corresponding to each of the occupied AOs in the atom.
—The double-zeta (DZ) basis set: it consists of two basis functions per atomic orbital and is thus twice as large as the minimal set. Here the word "*zeta*" is typically used for the exponent. In the same way, basis sets of triple zeta (TZ), quadruple zeta (QZ)...etc. quality can be constructed. Besides the increased flexibility at the HF-level the effects of radial electron correlation require the use of DZ or better basis set quality.
—The split-valence (SV) basis set: This basis set is minimal for the inner-shell AOs and double-zeta for the valence AOs.
—The double zeta plus polarization basis set: in this basis set polarization functions are added to a double-zeta basis set (DZ+P). Polarization functions—corresponding to atomic orbitals with higher l quantum number than those corresponding to the occupied atomic orbitals in the atomic ground state. Polarization functions are needed to increase the flexibility of the AO-basis for atoms in a non-spherical environment at the HF-level, e.g., when forming a chemical bond, and also to allow for angular correlation effects.

2.2. Electron Correlation Methods

In the Hartree-Fock approximation, one solves equations for the behavior of each electron in the averaged field of the remaining $(n-1)$ electrons. Unfortunately, electrons respond to each other in an instantaneous manner via Coulomb's law. That is, the motion of the $n(n-1)/2$ pairs of electrons are correlated, and it is precisely this *electron correlation* which is neglected in the HF model. The *correlation energy* is conveniently defined as

$$E_{corr} = E_{exact} - E_{HF} \tag{2.27}$$

i.e., the difference between the (nonrelativistic) exact energy and the HF limit energy. The correlation effect is the theoretical concept introduced into quantum chemistry as a tool that aims to correct the deficiency of the independent electron models, specifically the Hartree-Fock model. The first deficiency of the HF description consists in the

fact that two electrons with opposite spins are not prevented from occupying the same region of space at the time. Then the Coulomb interaction $1/r_{ij}$ between electrons i and j becomes infinite, which is energetically unfavorable. This defect of the correlation of motion of electrons means that the "Coulomb hole" that surrounds each one of the electrons is not properly respected. In contrast, the probability density of finding two electrons with the same spin at a point r is zero. This type of electron correlation gives rise to the "Fermi hole". It is a direct consequence of the Pauli principle, which the HF function obeys. Nevertheless, the neglect of correlation between electrons of opposite spin leads to a number of quantitative deficiencies in the description of electronic structure. The effect associated with the Coulomb induced correlation between the motion of electrons is referred to as dynamical correlation. However, a quantitative understanding of electronic correlations is a necessary contribution to accurate *ab initio* calculations for solids as well as for polymers. Here, the short-range electron correlations i.e., dynamical correlations play an especially important role. Therefore, this type of correlation is of central interest to us. It dominates in closed shell molecules, which usually may be well described within the restricted HF formalism by the single determinant that serves as a reference function. Another deficiency of the spin-restricted closed-shell HF function is that it usually does not dissociate correctly when nuclei are moved to infinite separation. For example, the very large error of several eV obtained at the asymtotic limit when the hydrogen molecule is dissociated, i.e., instead of dissociation into two neutral H atoms only the separated ion pair $H^{\oplus} - H^{\ominus}$ can be described by the (symmetry-broken spin-restricted) HF solution. The correlation energy arising from long-range correlation effects, such as observed for molecular dissociation, is often referred to as non-dynamical (static) correlation, and can usually be dealt with by multiconfigurational SCF techniques (MCSCF). In this thesis we are mainly concerned with the dynamical correlation.

However, there are several existing theoretical methods for treating the electron correlation problem starting from a HF single determinant wave-function. One of the (formally) simplest theoretical methods is full configuration interaction (FCI) method in which the wave-function is the best linear combination of all possible configuration state functions within a given basis set. In practice it is realized, however, that FCI rapidly becomes impractically time consuming if there are more than a few electrons in the system. The CI expansion is, therefore, conventionally truncated and its most popular version includes only single and double substitutions and which is called the singles and doubles CI (CISD) method. This method is variational but not size-extensive. The size-extensivity becomes more important with increasing number of electrons. Therefore, the second range of approximate correlation methods is based on many-body perturbation theory (MBPT) which is size-extensive at any order but not variational. This method treats the correlation part of Hamiltonian as a perturbation on the HF part and truncates the energy expansion at some order. A generalization of MBPT is coupled-cluster (CC) theory which combines the size-extensivity of MBPT with the infinite summation of CI. The key idea of the CC method is the use of an exponential ansatz for the wavefunc-

tion, which permits the inclusion of a greatly increased number of excited configurations relative to the number of unknown coefficients (t-amplitudes) and hence sums the correlation contributions from these configurations in a very efficient way. The exponential wavefunction ansatz also ensures the extensivity of the CC method. However, CC theory is an infinite-order perturbation method, and, unlike MBPT, is independent of the choice of the unperturbed Hamiltonian.

2.2.1. Configuration Interaction

The configuration interaction (CI) method is the oldest treatment for recovering dynamical correlation [30]. In this method the exact wave-function can be written as a linear combination in terms of configuration state functions (CSF; spin- and space-symmetry-adapted linear combinations of Slater-determinants),

$$\Psi = \sum_R C_R \Phi_R + \sum_I C_I \Phi_I \tag{2.28}$$

where C_R and C_I are the variational parameters and Φ_R denotes the so-called reference configuration functions. In most cases the first sum in equation (2.28) contains just one term, and the expansion is called "single-reference CI" or simply "CI" expansion. In that case the reference function is usually the HF function Φ_0. If there is more than one reference function then the expansion is referred to as multireference CI (MRCI) expansion. The indices R and I used in (2.28) are collective indices denoting the orbital structure of the individual CSFs. The orbital structure of the CSFs is usually defined by stating how they differ from the reference configurations Φ_R. A single excitation differs by one orbital from the reference configuration, a double excitation by two, and so on. In a FCI wave-function configurations with all possible excitations with respect to the reference ground state are included and we can write the equation (2.28) in intermediate normalization $< \Phi_0 | \Psi_0 >= 1$ in the following form:

$$\begin{aligned} \Psi_0 &= \Phi_0 + \sum_{i,a} C_i^a \Phi_i^a + \sum_{\substack{i<j \\ a<b}} C_{ij}^{ab} \Phi_{ij}^{ab} + \sum_{\substack{i<j<k \\ a<b<c}} C_{ijk}^{abc} \Phi_{ijk}^{abc} + \cdots \\ &= (1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \cdots)\Phi_0 \end{aligned}$$

where the index $i, j...$ and $a, b...$ denote occupied and unoccupied MOs respectively, in Φ_0. The excitation operators are defined

$$\hat{T}_1 = \sum_{i,a} t_i^a a_a^\dagger a_i \tag{2.29}$$

$$\hat{T}_2 = \sum_{\substack{i>j> \\ a>b>}} t_{ij}^{ab} a_a^\dagger a_i a_b^\dagger a_j \tag{2.30}$$

$$\hat{T}_k = \sum_{\substack{i>j>k... \\ a>b>c...}} t_{ijk...}^{abc...} a_a^\dagger a_i a_b^\dagger a_j a_c^\dagger a_{k...} \tag{2.31}$$

where a_i,a_j,... mean annihilation operator on orbital $i, j, ...$, while $a_a^\dagger$,$a_b^\dagger$, ... mean creation operators on orbital $a, b, ...$ All coefficients are varied to minimize the expectation value of the energy

$$(E_{CI} = \frac{< \Psi_{CI}|\hat{H}|\Psi_{CI} >}{< \Psi_{CI}|\Psi_{CI} >}) \tag{2.32}$$

which leads to the following simple eigenvalue equation

$$(\mathbf{H} - E\mathbf{1})\mathbf{C} = \mathbf{0} \tag{2.33}$$

in the case of orthonormal CSFs, i.e., $< \Psi_s|\Psi_t >= \delta_{st}$. The matrix elements of $\mathbf{H}$ are defined by

$$H_{st} =< \Phi_s|\hat{H}|\Phi_t > \tag{2.34}$$

and these Hamiltonian matrix elements H_{st} are linear combinations of one- and two-electron integrals, cf. the so-called Slater-Condon rules for their evaluation [31].
The FCI method is size-extensive however, the method is not practical except for very small systems because of the very large number of determinants, e.g., for N electrons and n basis function one can construct $\binom{2n}{N}$ determinants. Nevertheless, FCI calculations provide a useful benchmark for approximate scheme.
To obtain a computationally viable scheme one usually truncates the CI expansion for the wave function. If we take the SCF wave function as a zeroth-order wave function in perturbation theory, then all triple and higher excitations make no contribution to the wave function to first order. For this reason, CI including all single and double excitations (CISD) became the goal of a number of the standard theoretical methods. It has been found [32] that CISD accounts for the major correlation contributions to Ψ. The singly excited configurations contribute significantly to one-electron properties, whereas the doubly excited configurations have the largest role in correcting the HF energy. CISD is variational, but it is not size-extensive. In applications, size-extensivity is generally regarded as being more important than provision of an energy upper bound, so CISD results are usually modified by a simple correction, introduced by Langhoff and Davidson [33], which makes the energies approximately size extensive, but no longer variational:

$$E_{correction} = (1 - C_0^2)\Delta E_{CISD} \tag{2.35}$$

Here ΔE_{CISD} is the correlation energy at the CISD level and C_0 is the coefficient of the HF wave function in the CISD expansion.
For finite systems, e.g., atoms and molecules, the CI approach may be considerably improved by using a multi-configurational zeroth-order wavefunction (MRCI), which is best obtained from a multi-configurational self-consistent field calculation (MCSCF). Since this approach has not been extended to infinite system, e.g., polymers, we will not discuss this method any further.

2.2.2. Second–Order Møller–Plesset Perturbation Theory

The most economical general correlation methods are based on the perturbation theory of *Møller* and *Plesset* [34]. In this method, the Hamiltonian operator of a molecule containing N-electrons occupying N-spin orbitals χ_i is divided into two parts, an unperturbed Hamiltonian $\hat{H}_0$ and a perturbation $\lambda\hat{H}_1$.

$$\hat{H} = \hat{H}_0 + \lambda\hat{H}_1, \qquad \hat{H}_0 = \sum_i \hat{h}_i + \hat{V}_{HF}, \qquad \hat{H}_1 = \sum_{i<j} \frac{1}{r_{ij}} - \hat{V}_{HF} \tag{2.36}$$

The wavefunction and energy are expanded in a similarly way and it is assumed that the zeroth-order wavefunctionΨ_0 is an eigenfunction of $\hat{H}_0$ with the eigenvalue E_0:

$$\Psi = \Psi_0 + \lambda\Psi_1 + \lambda^2\Psi_2 + \cdots \tag{2.37}$$

$$E = E_0 + \lambda E_1 + \lambda^2 E_2 + \cdots \tag{2.38}$$

By inserting (2.36), (2.37) and (2.38) into the Schrödinger equation and collecting terms of the same order in λ we get the following hierarchy of equations up to second order:

$$\hat{H}_0\Psi_0 = E_0\Psi_0 \tag{2.39}$$

$$(\hat{H}_0 - E_0)\Psi_1 = (E_1 - \hat{H}_1)\Psi_0 \tag{2.40}$$

$$(\hat{H}_0 - E_0)\Psi_2 = (E_1 - \hat{H}_1)\Psi_1 + E_2\Psi_0 \tag{2.41}$$

We may assume that the perturbed wave-functions are orthogonal to the zeroth-order function, $< \Psi_0|\Psi_i >= \delta_{i0}$, which leads to the so-called intermediate normalization of the total wave-function: $< \Psi|\Psi_0 >= 1$. Using this normalization we obtain the following expressions for the energies up to second order:

$$E_0 =< \Psi_0|\hat{H}_0|\Psi_0 > \tag{2.42}$$

$$E_1 =< \Psi_0|\hat{H}_1|\Psi_0 > \tag{2.43}$$

$$E_2 =< \Psi_0|\hat{H}_1|\Psi_1 > \tag{2.44}$$

The first-order wave-function appears in the expression for the second-order energy. It is obtained by solving the equation (2.40). In Møller–Plesset perturbation theory the unperturbed Hamiltonian $\hat{H}_0$ is chosen to be a sum of Fock-operators acting on each electron. The zeroth-order energy is immediately obtained as the sum of the eigenvalues (orbital energies) for the occupied spin orbitals. It follows that the sum of the zeroth- and first-order energy equals the HF energy. In order to solve the first-order equation, we expand the first-order wave-function in determinants Φ_μ:

$$\Psi_1 = \sum_\mu C_\mu\Phi_\mu \tag{2.45}$$

where in case of MP2 the sum runs over excited determinants with respect to the HF ground state. We notice that all Φ_μ are eigenfunctions of $\hat{H}_0$ with eigenvalues E_μ equal to the sum of the orbital energies of the spin-orbitals occupied in the given determinant. By inserting equation (2.45) into the (2.41) get the following expression for the first-order expansion coefficients:

$$C_\mu = -\frac{<\Phi_\mu|\hat{H}_1|\Psi_0>}{E_\mu - E_0} \tag{2.46}$$

We notice that the numerator contains the interaction between the configuration Φ_μ and the HF reference function Ψ_0. Thus only those configurations, for which this element is non-zero need to be included in the expansion of the first-order wave function (2.45). We know from the Slater rules that they are the doubly excited configurations. Singly excited configuration will not contribute due to the Brillouin theorem, which states that there is no interaction between the closed-shell HF wavefunction and singly excited configurations.

$$\Psi_1 = \sum_{\substack{i>j \\ a>b}} C_{ij}^{ab} \Psi_{ij}^{ab} \tag{2.47}$$

where i, j are occupied and a, b virtual spin-orbitals. According to equation (2.46) the coefficients in second-order Møller–Plesset perturbation theory are given by:

$$C_{ij}^{ab} = -\frac{<\Psi_0|\hat{H}|\Phi_{ij}^{ab}>}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j} \tag{2.48}$$

and the second order energy by:

$$E_2 = -\sum_{\substack{i>j \\ a>b}} \frac{|<\Psi_0|\hat{H}|\Phi_{ij}^{ab}>|^2}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j} \tag{2.49}$$

The energy expression (2.38), may be terminated at any desired order, and these energies have the property of size-extensivity, but are not variational. The complexity and cost of computing the energy terms in this expansion increases rapidly with the order, i.e., standard calculations only use second, third or fourth order (MP2, MP3 or MP4).

2.2.3. Coupled Cluster Method

The coupled cluster (CC) method [10] has emerged in recent years as a powerful tool for treating electron correlation to high accuracy for small- to medium-sized atoms and molecules. The advantage of this method is the size-extensivity no matter what truncation of the excitation level is employed, and no matter which terms are dropped from the resulting equations. The single reference CC method [8] has been particular successful for describing most closed-shell states. The method is based on the exponential ansatz:

$$\Psi_{CC} = e^{\hat{T}}\Phi_0 = (1 + \hat{T} + \frac{1}{2!}\hat{T}^2 + \frac{1}{3!}\hat{T}^3 + \cdots)\Phi_0 \tag{2.50}$$

where the independent-particle reference Φ_0 is the closed-shell HF wave function composed of n occupied (labelled by $i, j, k, ...$) spin orbitals. The operator $\hat{T}$ is a sum of the excitation operators of different types such as single excitations $\hat{T}_1$, double excitations $\hat{T}_2$, and triple excitations $\hat{T}_3$ and so on. We may truncate the summation at m-tuple excitations $\hat{T}_m$

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \cdots + \hat{T}_m \tag{2.51}$$

If m equals the maximum allowed number of excitations, CC(m) becomes identical to FCI. The operator $\hat{T}$ is usually truncated after double excitations which defines the coupled-cluster singles and doubles (CCSD) [35, 36, 37] method.

$$\Psi_{CCSD} = e^{(\hat{T}_1+\hat{T}_2)}\Phi_0 \tag{2.52}$$

If we insert the wave function ansatz into the Schrödinger equation

$$(H - E_{CCSD})\Psi_{CCSD} = (H - E_{CCSD})e^{(\hat{T}_1+\hat{T}_2)}\Phi_0 = 0 \tag{2.53}$$

then projecting against the reference, singly, and doubly excited states, we obtain a set of equations sufficient for determining the t_i^a and t_{ij}^{ab} coefficients:

$$< \Phi_0|(H - E_{CCSD})(1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2}\hat{T}_1^2)|\Phi_0 >= 0 \tag{2.54}$$

$$< \Phi_i^a|(H - E_{CCSD})(1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2}\hat{T}_1^2 + \hat{T}_1\hat{T}_2 + \frac{1}{3!}\hat{T}_1^3)|\Phi_0 >= 0 \tag{2.55}$$

$$< \Phi_{ij}^{ab}|(H - E_{CCSD})(1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2}\hat{T}_1^2 + \hat{T}_1\hat{T}_2 + \frac{1}{3!}\hat{T}_1^3 + \frac{1}{2}\hat{T}_2^2 + \frac{1}{4!}\hat{T}_1^4)|\Phi_0 >= 0, \tag{2.56}$$

The expansions on the right-hand site terminate after the quadruple excitations since the Hamiltonian contains only one- and two-particle operators. The number of equations corresponds exactly to the number of coefficients. Finally, the closed-shell CCSD energy is given as,

$$E_{CCSD} =< \Phi_0|H|\Phi_0 > + \sum_{i,a} f_{ia}t_i^a + \sum_{\substack{i>j>\\ a>b>}} < ij||ab > (t_{ij}^{ab} + t_i^a t_j^b - t_i^b t_j^a) \tag{2.57}$$

where f_{ia} and $< ij||ab >$ are Fock matrix elements and antisymmetrized two-electron integrals, respectively. The computational cost of this method rises asymptotically with the sixth power of the basis set dimension, a scaling which is identical to that associated with third-order MBPT and the configuration interaction singles and doubles (CISD) method. Although the CCSD method is more complete than its configuration interaction (CISD) counterpart, it is often not sufficiently accurate to allow molecular properties to be calculated at a high level of accuracy (within 1% of the full CI limit). In principle, the solution of this problem is to include more terms in $\hat{T}$. However, this becomes very expensive, as even CCSDT [38, 39] calculations scale with the eighth

power of the basis set size and are feasible only for small molecules. A practical way to achieve increased accuracy is to augment the CCSD energy with the correction term that approximates the effect of the T_3 operator while avoiding the most expensive steps in CCSDT calculations. These criteria are satisfied by the single, double, and perturbative triple excitations coupled-cluster $CCSD(T)$ method which was first developed by Raghavachari *et. al.* [40] as a computationally inexpensive way to incorporate the effects of connected triple excitations in the coupled-cluster procedure. The CCSD(T) method is less expensive than the CCSDT method because connected T_3 terms are not included directly in the exponential wave function. Instead, the CCSD(T) method approximates the effect of connected triples terms with a perturbative energy correction, which is simply added to the single and double excitations coupled-cluster (CCSD) energy to obtain the CCSD(T) energy. This correction is obtained using the converged single and double excitation coefficients from a CCSD wave-function. Therefore, the CCSD(T) procedure partially accounts for both interactions between single and triple excitations and interactions between double and triple excitations. For a more detailed discussion, the reader may refer to Scuseria's earlier papers [41, 42, 43].

2.2.4. Density Functional Theory

Density Functional Theory (DFT) nowadays is probably the most often used approach of computational quantum chemistry for the study of ground state molecular properties. Here we present the basic idea of this method. The foundation of the DFT has been given with the formulation of the Hohenberg–Kohn (HK) theorem [2]. According to the HK theorem the total electronic energy E is a functional of the electron density

$$E = E[\rho] \tag{2.58}$$

and any trial density $\tilde{\rho}(\mathbf{r})$ obeying equation (2.59) (where N is the total number of electrons)

$$N = \int \tilde{\rho}(\mathbf{r}) d\mathbf{r} \tag{2.59}$$

fulfills

$$E[\tilde{\rho}] \geq E[\rho] \tag{2.60}$$

i.e., a variational principle exists for the true energy functional. The large importance of the HK theorems is that one does not calculate the full N-body wave function but only the total electron density ρ in order to obtain all ground-state properties. However, they do not give the relevant functionals, and to date there does not exist any general exact functionals. Practical applications of the HK density-functional formalism concentrate on calculating the electron density ρ and the total electronic energy E as accurately as possible but, due to the lack of exact functionals, by using certain approximations. A very useful approach was presented by Kohn-Sham (KS) [3], who reformulated the problem of calculating the total electronic energy E as a functional of the electron density

ρ as that of solving a set of single-electron Schrödinger-like equations. In this method one starts with the functional

$$E[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho] \tag{2.61}$$

By writing the density as

$$\rho = \sum_i |\chi_i|^2 \tag{2.62}$$

and differentiating equation (2.61) with respect to the density, subject to the constraint that the KS orbitals χ_i remain orthonormal, one can derive the following KS equation:

$$[-\frac{1}{2}\nabla^2 + \upsilon_{eff}]\chi_i = \varepsilon_i \chi_i \tag{2.63}$$

where the KS effective potential is defined by

$$\upsilon_{eff}(\mathbf{r}) = \upsilon(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \upsilon_{xc}(\mathbf{r}) \tag{2.64}$$

with the exchange-correlation potential

$$\upsilon_{xc}(\mathbf{r}) = \frac{\delta E_{xc}(\rho)}{\delta \rho(\mathbf{r})} \tag{2.65}$$

The exact ground-state density $\rho(\mathbf{r})$ can be found from the KS orbitals χ_i according to equation (2.62). The total energy can be determined from the formula

$$E = \sum_i^N \varepsilon_i - \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{xc}[\rho] - \int \upsilon_{xc}(\mathbf{r})\rho(\mathbf{r}) d\mathbf{r} \tag{2.66}$$

Here

$$\sum_i^N \varepsilon_i = \sum_i^N < \chi_i | -\frac{1}{2}\nabla^2 + \upsilon_{eff}(\mathbf{r}) | \chi_i > \tag{2.67}$$

These equations (2.62), (2.63) and (2.64) must be solved self-consistently. One begins with a guessed ρ, constructs υ_{eff} from (2.64), and then finds a new ρ from (2.62) and (2.63). Finally the total energy can be computed from (2.66).
In toto, KS equations have the same form as the HF equations, but KS-DFT is distinguished from HF theory in its capacity to fully incorporate the electron-correlation effects. However, since the precise functional dependence of υ_{xc} on ρ is not known, one has to resort to approximations. The simplest possible approximation is the local density approximation (LDA) which consists of replacing the exchange-correlation energy $E_{xc}[\rho]$ by

$$E_{xc} = \int \varepsilon_{xc}(\rho)\rho(\mathbf{r}) d\mathbf{r} \tag{2.68}$$

where $\varepsilon_{xc}(\rho)$ is the exchange and correlation energy per electron of a homogeneous electron gas of density ρ. Then

$$\upsilon_{xc}(\mathbf{r}) = \frac{\delta}{\delta\rho}E_{xc} = \varepsilon_{xc} + \rho\frac{d}{d\rho}\varepsilon_{xc} \tag{2.69}$$

depends only on $\rho(\mathbf{r})$ at position $\mathbf{r}$ and the KS equations take a simple form. Before the KS-LDA method was introduced, the X_α-method was proposed by Slater [44], in which the correlation contribution to E_{xc} is neglected and the exchange contribution is taken as

$$E_{x\alpha} \approx \alpha \int \rho^{\frac{4}{3}}(\mathbf{r})d\mathbf{r} \tag{2.70}$$

In fact that if the correlation is ignored in LDA the resulting KS equation is precisely the X_α equation with $\alpha = \frac{2}{3}$. The LDA approximation is reasonable in many cases, but a significant improvement of accuracy was achieved by introducing the gradient of the density

$$E_{xc}[\rho] = \int d\mathbf{r}\rho(\mathbf{r})\varepsilon_{xc}\Big(\rho(\mathbf{r}); \nabla\rho(\mathbf{r})\Big) \tag{2.71}$$

This is the so-called "non-local" approximation or generalized gradient approximations (GGA), where the unknown functional is approximated by an integral over a function that depends only on the density and its gradient at a given point in space. In addition to LDA and GGA some other important improvements have been made in recent years and they are well summarized in the reference [45].

3. Methods for Polymers and Solids

Currently, most of the *ab initio* electronic structure calculations of solids and polymers are based on density functional theory (DFT), which in practise employs the local-density approximation (LDA) [2, 3]. The DFT method approximately includes electron correlation and often gives better results than Hartree-Fock (HF) theory. However, the attractiveness of this method for practical calculations results mainly from the speed with which the computations can be carried out, and the main deficiency is that no systematic improvement towards the exact result is possible.
On the other hand, in the wave-function-based approach, one can improve the calculation systematically by enlarging the basis set and by including more terms in the expansion of the wave-function, however, at the price of a considerably higher computational cost. In this thesis, we will mainly discuss and apply such a wave-function-based methods for non-metallic systems.
A typical quantum-chemical investigation of polymers or solids, employing a wave-function-based approach, begins with a Hartree-Fock (HF) calculation which provides an initial mean-field description of the system. Then, it is improved systematically by considering virtual excitations from the HF wave-function in order to account for electron correlations. The task appears to be fraught with problems considering the infinite number of degrees of freedom. During the last couple of decades, the HF problem has been solved for the first time for infinite periodic systems. The state of the art in these methods is represented by the CRYSTAL program [46]. In this program the electron orbitals are described by the Bloch orbitals, which are delocalized allover the infinite crystal [47]. As an alternative representation to the Bloch orbitals, the use of localized Wannier orbitals was proposed by Wannier [48]. In fact, the two types of orbitals are related by a unitary transformation, hence they differ only in terms of their practical implementation.
The localized-electron picture helps to handle the problem of infinities at the correlated level as well. The electron correlation effects are "local" in the sense that they are important only among the electrons which are nearby. Thus in the localized representation one can describe electron correlation by means of a finite number of virtual excitations of the HF state in which one of the electrons involved will be in the reference cell and other ones could be in the reference cell or in a unit cell close by. It is intuitively obvious that an *ab initio* treatment of electron correlations on large or infinite systems will converge much faster with localized orbitals as compared to delocalized orbitals. There-

fore, for an *ab initio* treatment of electron correlations, one could in principle always transform the Bloch orbitals to a localized representation using a suitable localization procedure [13]. During the last years, in our group a HF approach was developed which allows the direct determination of Wannier-type orbitals within the SCF process [49]. In this Wannier-orbital-based method, instead of describing the electrons in terms of itinerant Bloch orbitals, one describes them in terms of mutually orthogonal orbitals localized within individual unit cells constituting the infinite solid. It is noteworthy that the Wannier-type orbitals are pseudo-canonical within the reference cell, i.e., they are not the most localized orbitals possible. In the localized electron picture of the solid, one usually needs to describe only the electrons of one unit cell of the solid, the unit cells of the rest of the infinite solid being just the copies of that cell. Therefore, in order to obtain the HF wave function of the whole solid, one needs to solve the HF equations of the electrons of just one unit cell in the field of the rest of the system. Since the purpose of this chapter is to demonstrate the present state of the method which has been used for polymers, in the following sections, first, we will describe the Wannier-orbital-based Hartree-Fock method in detail, then the related correlation methods which have already been mentioned in the introduction.

3.1. Wannier-orbital-based Hartree-Fock method

The nonrelativistic many-electron Hamiltonian of a periodic infinite system can be written as:

$$H = -\frac{1}{2}\sum_i \nabla_i^2 - \sum_i \sum_I \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \sum_{i>j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{I>J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \tag{3.1}$$

where the $\mathbf{r}_i$ denotes the position vectors of the ith electron while $\mathbf{R}_I$ and Z_I denote the position and charge of the Ith nucleus of the lattice, respectively. The last term representing the nucleus-nucleus interaction will make a constant contribution to the energy per unit cell and will not effect the dynamics of the electrons. To solve the HF problem of an infinite periodic system in the Wannier representation we adopted the embedded-cluster approach. In this approach, the infinite system is devided into a reference unit cell called the "central cluster" ($\mathcal{C}$), and its "environment" ($\mathcal{E}$) consisting of the rest of the infinite number of unit cells. Thus, we envision $\mathcal{C}$ as a cluster embedded in the field of the rest of the infinite system. Since the translational symmetry requires that the orbitals localized in two different unit cells be identical to each other (except for their location), it is sufficient for us to know the orbitals of the central cluster only, whereas the orbitals of all other cells can be generated from them by simple translation operations:

$$\alpha(\mathbf{R_i} + \mathbf{R}_j) = T(\mathbf{R}_i)\alpha(\mathbf{R}_j) \tag{3.2}$$

$\alpha(\mathbf{R}_j)$ denotes the α-th orbital in the unit cell located at position $\mathbf{R_j}$ of the lattice. $T(\mathbf{R_i})$ represents the operator which performs a translation by the vector $\mathbf{R}_i$. However,

to develop the theory further, we make assumptions that the infinite system under consideration is of closed-shell type and that a single Slater determinant represents a reasonable approximation to its ground state. Moreover, we assume that the same spatial orbitals represent both spin projections of a given shell, i.e., we confine ourselves to spin-restricted HF theory. With the preceding assumptions, the total energy of the system then can be written as

$$\begin{aligned} E_{HF} &= 2\sum_i < i|\hat{T}|i > +2\sum_i < i|\hat{U}|i > \\ &+ \sum_{i,j}(2 < ij|ij > - < ij|ji >) + E_{nuc} \end{aligned} \tag{3.3}$$

Here $|i>$ and $|j>$ denote the occupied spatial orbitals assumed to form an orthonormal set, $\hat{T}$ denotes the kinetic energy operator, $\hat{U}$ denotes the interaction of the electrons of $\mathcal{C}$ with the nuclei of the whole of the system, E_{nuc} denotes the nucleus-nucleus interaction energy, and $< ij|ij >$, etc. represent the interactions of the electrons with each other. Using translational symmetry one can rewrite the energy expression of equation (3.3) as

$$\begin{aligned} E_{HF} &= \lim_{N\to\infty} N\Big\{2\sum_{\alpha=1}^{n_c} < \alpha(\mathbf{0})|\hat{T}|\alpha(\mathbf{0}) > +2\sum_{\alpha=1}^{n_c} < \alpha(\mathbf{0})|\hat{U}|\alpha(\mathbf{0}) > \\ &+ \sum_{\alpha,\beta=1}^{n_c}\sum_{j=1}^{N}(2 < \alpha(\mathbf{0})\beta(\mathbf{R}_j) \mid \alpha(\mathbf{0})\beta(\mathbf{R}_j) > \\ &- < \alpha(\mathbf{0})\beta(\mathbf{R}_j) \mid \beta(\mathbf{R}_j)\alpha(\mathbf{0}) >) + E_{nuc}\Big\} \end{aligned} \tag{3.4}$$

$\alpha(\mathbf{0})$ denotes an orbital centered in the reference cell. Each unit cell comprises n_c doubly occupied orbitals. If we require that the energy of equation (3.4) be stationary with respect to changes of the orbitals in the reference cell, subject to the orthogonality constraint, we are led to the Hartree-Fock equations:

$$\left(\hat{T} + \hat{U} + 2\sum_\beta \hat{J}_\beta - \sum_\beta \hat{K}_\beta\right)\alpha(\mathbf{0}) = \epsilon_\alpha|\alpha(\mathbf{0}) > \tag{3.5}$$

where $\hat{J}$ and $\hat{K}$—the conventional Coulomb and exchange operators, respectively—are defined as

$$\hat{J}_\beta\alpha(\mathbf{0}) = \sum_j < \beta(\mathbf{R}_j)|\frac{1}{r_{12}}|\beta(\mathbf{R}_j) > \alpha(\mathbf{0}) \tag{3.6}$$

$$\hat{K}_\beta\alpha(\mathbf{0}) = \sum_j < \beta(\mathbf{R}_j)|\frac{1}{r_{12}}|\alpha(\mathbf{0}) > \beta(\mathbf{R}_j) \tag{3.7}$$

where the terms $\hat{U}$, $\hat{J}$, and $\hat{K}$ involve infinite lattice sums. The eigenvectors of the Hartree-Fock operator above in equation (3.5) will be orthogonal to each other, of course.

However, in general, these solutions of equation (3.5) would not be localized, nor would they be orthogonal to the orbitals of any other unit cell. This is because the orbitals centered in any other unit cell are obtained from those of the reference cell using a simple translation operation as defined in equation (3.2), which does not impose any orthogonality or localization constraint upon them. Since our aim is to obtain the Wannier-type functions of the infinite solid, i.e., all the orbitals of the solid must be localized and orthogonal to each other, we will have to impose these requirements explicitly upon the eigenspace of equation (3.5). This can most simply be accomplished by including in equation (3.5) the projection operators corresponding to the orbitals centered in the unit cells in a (sufficiently large) neighborhood of the reference cell

$$\left(\hat{T}+\hat{U}+\sum_{\beta}(2\hat{J}_{\beta}-\hat{K}_{\beta})+\sum_{k>1}\sum_{\gamma}\lambda_{\gamma}^{k}|\gamma(\mathbf{R}_k)><\gamma(\mathbf{R}_k)|\right)\alpha(\mathbf{0})=\epsilon_{\alpha}\alpha(\mathbf{0}) \tag{3.8}$$

where $k=1$ refers to the reference cell for which the orbitals are to be evaluated. In equation (3.8) the first three terms constitute the canonical HF operator, while the last term is a projection operator, that makes the orbitals localized in $\mathcal{C}$ orthogonal to those localized in the unit cells in the immediate neighborhood of $\mathcal{C}$ by means of infinitely high shift parameters $\lambda_{\gamma}^{k}\rightarrow\infty$. These neighborhood unit cells, the origins of which are labelled by lattice vectors $\mathbf{R}_k$, are collectively referred to as $\mathcal{N}$. The projection operators along with the shift parameters play the role of a localizing potential in the Fock matrix, and once self-consistency has been achieved, the occupied eigenvectors of equation (3.8) are localized in $\mathcal{C}$, and are orthogonal to the orbitals of $\mathcal{N}$–thus making them Wannier-type functions.

In practical calculations using this method we partition the whole system into three parts which are shown in figure (3.1) for a square lattice. The part $\mathcal{C}$ is the reference unit cell (central cluster). The modified HF equations (3.8) can be solved for orbitals in this region. The part $\mathcal{N}$ is the short-range environment, i.e., neighbourhood of the reference cell which contributes to $\hat{U}$, $\hat{J}$, $\hat{K}$ and the projection operators. The part $\mathcal{R}$ is the long-range environment, i.e., rest of the infinite system and its exchange interaction with the central cluster as well as orthogonality constraints are ignored. Thus it contributes only to $\hat{U}$ and $\hat{J}$. The partitioning of the system is system-dependent and has to be adjusted individually. For ionic and well localizable covalent systems typically up to the third-nearest neighbor unit cells are included in the short-range environment.
To solve equation (3.8) we adopted a linear-combination of atomic orbital (LCAO) formalism in which the orbitals localized in the reference cell are expanded as:

$$\alpha(\mathbf{0})=\sum_{p}\sum_{\mathbf{R_j}\in\mathcal{C}+\mathcal{N}}C_{p,\alpha}p(\mathbf{R}_j) \tag{3.9}$$

where $\mathbf{R}_j$ represents the location of the jth unit cell (located in $\mathcal{C}$ or $\mathcal{N}$) and $p(\mathbf{R}_j)$ represents a basis function centered in the $\mathbf{R}_j$. In practical calculation, for $p(\mathbf{R}_j)$ we adopted Gaussian lobe basis functions. Here p and higher angular momentum CGTFs

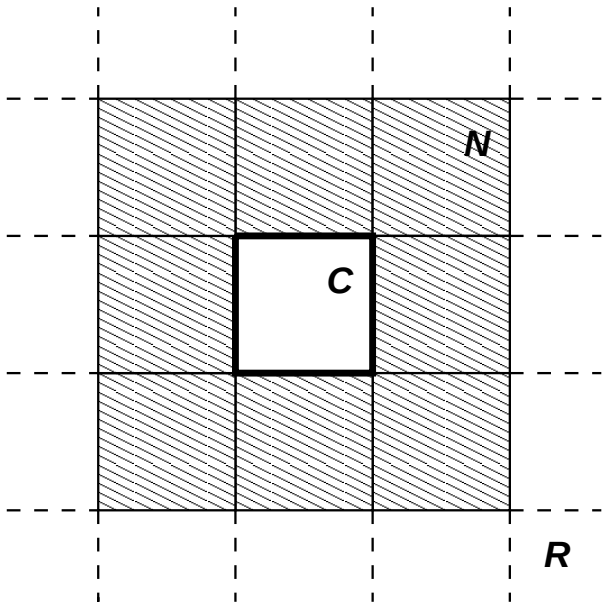

Figure 3.1.: Partitioning of the system.

correspond approximately to linear combinations of s-type basis functions displaced by a small amount from the location of the atom concerned. In order to account for the orthogonalization tails of the reference cell orbitals, we have to include in (3.9) the basis functions centered in $\mathcal{N}$ as well. Clearly, the translational symmetry of the crystal as expressed in equation (3.2) demands that the orbitals localized in two different unit cells have the same expansion coefficients $C_{p,\alpha}$, and differ only in the location of the centers of the basis functions. By substituting equation (3.9) in equation (3.8) we obtain the Hartree-Fock-Roothaan equations:

$$\sum_q F_{pq} C_{q,a} = \epsilon_a \sum_q S_{pq} C_{q,a} \tag{3.10}$$

The Fock matrix F_{pq} occurring in the equation above is defined as:

$$F_{pq} =< p|(\hat{T} + \hat{U} + 2\hat{J} - \hat{K})|q > + \sum_{k\in\mathcal{N}} \sum_{\gamma} \sum_{p'q'} \lambda_\gamma^k S_{pp'} S_{qq'} C_{p',\gamma} C_{q',\gamma} \tag{3.11}$$

The overlap matrix is given by:

$$S_{pq} =< p|q > \tag{3.12}$$

where unprimed functions p and q represent the basis functions corresponding to the orbitals of the reference unit cell $\mathcal{C}$ while the primed functions $p^{'}$ and $q^{'}$ denote the basis functions corresponding to the orbitals of $\mathcal{N}$. The matrix form of the HF equations (3.10) is a pseudo eigenvalue problem which can be solved iteratively to obtain the HF orbitals. Using these orbitals one can calculate total energy per unit cell as:

$$E_{cell} = 2trace\{(T + U + \frac{1}{2}(2J - K))D\} + E_{nuc-nuc} + \frac{1}{2}E_{nuc-nuc'} \tag{3.13}$$

where T, U, J, K and D denote the matrix representation of the corresponding operators. $E_{nuc-nuc}$ is the internuclear interaction energy for nuclei within the reference cell, whereas $E_{nuc-nuc'}$ is the interaction between the nuclei inside and outside the reference cell. D is the electron density matrix and defined as:

$$D_{pq} = \sum_{\alpha} C^{*}_{p,\alpha} C_{q,\alpha} \tag{3.14}$$

In the above equations the main aspect, that makes the problem of an infinite system different from the problem of a molecule is the evaluation of the infinite lattice sums for the electron-nucleus and electron-electron interaction parts of the Coulomb series by using some special techniques. Here, in the case of three dimensional system it can be calculated by using Ewald-summation techniques. In this method, one splits the lattice potential into a short-range part, whose contribution is rapidly convergent in $\mathbf{r}$ space, and a long-range part, which converges fast in $\mathbf{k}$ space. The details of this method are presented in Ref [50]. For polymers, we calculated it by using real-space based summation method. Furthermore, for polymers the matrix elements of the electron-nucleus interaction term and the matrix elements of Coulombic part of electron-electron repulsion term in equation (3.8) can be constructed as [51]:

$$U_{pq}(\mathbf{t}_{pq}) = -\sum_{j=-M}^{M} \sum_{A}^{atoms} \langle p(\mathbf{t}_{pq}) | \frac{Z_A}{|\mathbf{r} - \mathbf{R}_j - \mathbf{r}_A|} | q(\mathbf{0}) \rangle \tag{3.15}$$

$$J_{pq;rs}(\mathbf{t}_{pq}, \mathbf{t}_{rs}) = \sum_{j=-M}^{M} \langle p(\mathbf{t}_{pq}) r(\mathbf{t}_{rs} + \mathbf{R}_j) | \frac{1}{\mathbf{r}_1 - \mathbf{r}_2} | q(\mathbf{0}) s(\mathbf{R}_j) \rangle \tag{3.16}$$

Here the equation (3.16) by means of a coordinate transformation, can be brought into a form very similar to that of equation (3.15)

$$J_{pq;rs}(\mathbf{t}_{pq}, \mathbf{t}_{rs}) = \sum_{j=-M}^{M} \langle p(\mathbf{t}_{pq}) r(\mathbf{t}_{rs}) | \frac{1}{\mathbf{r}_1 - \mathbf{r}_2 - \mathbf{R}_j} | q(\mathbf{0}) s(\mathbf{0}) \rangle \tag{3.17}$$

where $|p(\mathbf{t}_{pq}) >$ and $|q(\mathbf{0}) >$ denote two basis functions separated by an arbitrary lattice vector $\mathbf{t}_{pq}$. $\mathbf{R}_j$ denotes the location of a unit cell, Z_A represents the nuclear charge of the A th atom, $\mathbf{r}_A$ represents its fractional coordinates, and the summation over A naturally runs over all the atoms in the unit cell i.e., $M \to \infty$. However, in practical calculations the contribution of the Coulomb series to the Fock matrix element is brought to convergence by choosing a "sufficiently-large" value M. The variable M clearly implies the inclusion of the Coulomb interaction of the reference cell electrons with those in up to its M-th nearest neighbours. Thus,the divergences inherent in the two terms will cancel each other owing to opposite signs when combined together to form the corresponding Fock matrix element. The total energy per unit cell will also be convergent if one uses the same value of M to evaluate the contribution of the nucleus-nucleus interaction

energy as well. The exchange interaction term is of short range and converges rapidly in the real space. Here we use a special truncation scheme.
Finally, we can summarize the HF method in terms of the following algorithmic steps: (1) Generate localized initial guess occupied orbitals for the reference cell. (2) From the reference cell orbitals generate the environment orbitals by using translation operations. (3)Construct the Fock matrix for the orbitals in the reference cell. (4) Solve the HF equations. (5) Compute the energy per unit cell. (6) Go to step (2) until convergence has been achieved. The correctness of this method has been demonstrated by applying it to different systems [52, 53, 54]. The results for polymers will be presented in the next chapter.

3.1.1. Wannier Orbitals Versus Bloch Orbitals

In most further applications of the wavefunctions obtained in the Hartree-Fock step, the use of Wannier-type functions instead of the original Bloch functions seems to be very promising. Since their introduction in 1937 [48], Wannier functions have often been used in many theoretical considerations of electronic properties of crystals. Here we briefly describe the construction of these functions.
It is well known, in the study of periodic crystalline solids the eigenfunctions of the Schrödinger equation with a periodic potential are usually the Bloch wave functions $\phi_{n\mathbf{k}}(\mathbf{r})$, characterized by the wave vector $\mathbf{k}$ and the band index n and can be written as:

$$\phi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}.\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}) \tag{3.18}$$

where the u's obey *periodic* boundary conditions over the elementary cell:

$$u_{n\mathbf{k}}(\mathbf{r}+\tau) = u_{n\mathbf{k}}(\mathbf{r}) \tag{3.19}$$

The Bloch functions are delocalized over entire infinite crystal. However, they can be localized to Wannier functions by unitary transformations. Namely, an equivalent set of Wannier functions $\mathcal{W}_n(\mathbf{r}-\mathbf{R})$ are defined in terms of the Bloch functions as the following:

$$\mathcal{W}_n(\mathbf{r}-\mathbf{R}) = \frac{1}{\upsilon(BZ)} \int_{BZ} d\mathbf{k} \phi_{n\mathbf{k}}(\mathbf{r}) e^{-i\mathbf{k}.\mathbf{R}} \tag{3.20}$$

where the integration goes over the first Brillouin zone (BZ), of volume $\upsilon(BZ)$. There exists, for each band n, a set of Wannier functions, all identical except for simple translations through lattice vectors $\mathbf{R}$. The Wannier functions centered around different lattice points form a complete set, which is orthogonal in the sence that

$$\int d\mathbf{r} \mathcal{W}_n^*(\mathbf{r}-\mathbf{R}) \mathcal{W}_{n'}(\mathbf{r}-\mathbf{R}') = \delta_{nn'}\delta_{\mathbf{R}\mathbf{R}'} \tag{3.21}$$

The normalization in equation (3.21) presupposes that the Bloch functions are normalized

$$\langle \phi_{n\mathbf{k}} | \phi_{n'\mathbf{k}'} \rangle = \delta_{nn'}\delta_{\mathbf{k}\mathbf{k}'} \tag{3.22}$$

It is clear that in equation (3.20), the Wannier functions are defined in terms of a unitary transformation performed on the occupied Bloch orbitals. However, they are not uniquely defined, due to the arbitrary freedom in the phases of the Bloch orbitals. In the case of an isolated band (i.e., a band that does not become degenerate with any other band anywhere in the BZ), the freedom in the choice of the Wannier functions corresponds to the freedom in the choice of the phases of the Bloch orbitals as a function of wave vector **k**. Thus the transformation is defined as

$$|u_{n\mathbf{k}}\rangle \rightarrow e^{i\phi_n(k)}|u_{n\mathbf{k}}\rangle \tag{3.23}$$

where ϕ_n is a real function of **k**. For a composite set of bands (i.e., bands that are connected between themselves by degeneracies, but separated from others by energy gaps), the corresponding freedom is

$$|u_{n\mathbf{k}}\rangle \rightarrow \sum_m U_{mn}^{(\mathbf{k})}|u_{m\mathbf{k}}\rangle \tag{3.24}$$

where U_{mn} is a unitary matrix that mixes the bands at wave vector **k**. Equation (3.23) can be regarded as a special case of equation (3.24) that results when the U are chosen diagonal. Thus, the most general operation that transforms the Bloch orbitals into Wannier orbitals can be written as:

$$\mathcal{W}_n(\mathbf{r}-\mathbf{R}) = \frac{1}{v(BZ)}\int_{BZ}\sum_m U_{mn}^{(\mathbf{k})}\phi_{m\mathbf{k}}(\mathbf{r})e^{-i\mathbf{k}.\mathbf{R}}d\mathbf{k} \tag{3.25}$$

However, the degree of localization is a subtle question. Here we present some reference just as being representative of such studies. Marzari and Vanderbilt [55] developed a very practical method for generating maximally localized Wannier functions for simple and composite bands in periodic systems. In this method the indeterminacy can be resolved by requiring that the total spread of the localized function is minimal. This criterion is in close analogy with the Boys-Foster [13] method for finite systems. Here one uses the spread defined through the conventional position operator. This technique was successfully applied to crystal systems within a general **k**-point scheme [55]. Some other methods have also developed which construct reasonable sets of Wannier functions, reducing the arbitrariness in the $U_{mn}^{(\mathbf{k})}$ with symmetry considerations and analyticity requirements [56], or explicitly employing projection techniques on the occupied subspace spanned by the Bloch orbitals [57]. However, nowadays, the use of localized Wannier-type orbitals is the best choice in many further studies as well as for wave-function-based electron correlation schemes of solids and polymers.

3.2. Correlated Methods for Polymers

It has already been discussed that, as for molecular systems also for infinite periodic systems the SCF method is only an approximation to the solution of the Schrödinger

equation. Recently, several attempts have been made to go beyond the SCF level and to include correlation effects. Since the size of a periodic polymer or crystal is infinite, correct scaling with the system size is an essential prerequisite for a correlated theory. The many-body perturbation theory in Møller-Plesset partitioning in any order and the coupled-cluster (CC) method have this property, and so they are appropriate tools for extended systems while the traditional truncated configuration interaction (CI) methods are not. However, when the full CI is used, the results are also size-extensive. Recently, the full CI has been interfaced with the localized Wannier orbitals by means of the incremental scheme and applied to a simple model system, i.e., the LiH chain [25] and three-dimensional LiH solid [58]. The CC method has also been employed to compute correlation corrections to the band structure of linear polymers with the help of localized Wannier functions at the linearized CCD (LCCD) and CCD level. [22] The most simplest suitable correlation method is Møller-Plesset second order perturbation theory (MP2) which was recently implemented for polymers by Bartlett et al. [21]. They studied the convergence of the corrections with lattice summation cutoff (N) and number of **k**-points taken in the first Brillouin zone in the integrations over the reciprocal lattice. Besides these methods the density functional theory was also implemented for polymers and applied to study various properties of polymers [89]. Since, at the present only a few correlated methods exist for electronic structure calculations on polymeric systems, we will briefly describe in the following sections the theoretical back ground of these methods.

3.2.1. Møller-Plesset Scheme for Infinite System

The MBPT method treats electron correlation as a perturbation to the independent-particle reference and the method truncated at any perturbation order is size-extensive. In this method, the HF ground-state wave-function as an unperturbed wave-function that can be constructed according to the HF theory as a normalized single determinant built up from doubly occupied one electron Bloch functions $\phi_n^{\mathbf{k}}$. Then the one-electron orbitals can again be expressed as a Bloch sum in the form:

$$\phi_n^{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{G}} \sum_{j=1}^{G} e^{-i\mathbf{k}.\mathbf{R}_j} \Lambda_n^{\mathbf{k}}(\mathbf{r} - \mathbf{R}_j) \tag{3.26}$$

where

$$\Lambda_n^{\mathbf{k}}(\mathbf{r} - \mathbf{R}_j) = \sum_{p=1}^{\nu} c_{p,n}^{\mathbf{k}} \chi_p(\mathbf{r} - \mathbf{R}_j - \mathbf{R}_p) \tag{3.27}$$

Here, G and ν are the number of cells and the number of basis orbitals per cell, respectively and it is assumed that the coefficients $c_{p,n}^{\mathbf{k}}$ are already known from the solution of the HF problem. From perturbation theory, we know that the exact total energy of the system can be expressed as

$$E = E^{(HF)} + E^{(2)} + E^{(3)} + \cdots \tag{3.28}$$

Since the total energy is infinite in an extended systems, we are more interested in the total energy per unit cell, which is defined as

$$E_{uc} = \lim_{N\to\infty} \frac{E(N)}{N} = E_{uc}^{HF} + E_{uc}^{(2)} + E_{uc}^{(3)} + \cdots \tag{3.29}$$

for which the expression of E_{uc}^{HF} has already been given in equation (3.13). The energy expression (3.29), may be terminated at any desired order, here we focus on the second-order correction. It is already known that the second-order energy in Møller-Plesset partitioning (MP2) can be written as [12]:

$$E^{(2)} = \frac{1}{4} \sum_{\bar{I}\bar{J}\bar{A}\bar{B}} \frac{|\langle \bar{I}\bar{J}|r_{12}^{-1}(1-\hat{P})|\bar{A}\bar{B}\rangle|^2}{\epsilon_{\bar{I}}^{HF} + \epsilon_{\bar{J}}^{HF} - \epsilon_{\bar{A}}^{HF} - \epsilon_{\bar{B}}^{HF}} \tag{3.30}$$

where $\bar{I}$,$\bar{J}$ and $\bar{A}$,$\bar{B}$ denote the occupied and unoccupied spin orbitals, respectively, in the HF ground state of the system. Using I, J, A, and B, to denote the corresponding spatial orbitals of $\bar{I}$,$\bar{J}$, $\bar{A}$ and $\bar{B}$, respectively, then for a closed-shell systems, equation (3.30) can be rewritten as

$$E^{(2)} = \sum_{IJAB} \frac{2|\langle IJ|r_{12}^{-1}|AB\rangle|^2 - Re[\langle IJ|r_{12}^{-1}|AB\rangle\langle BA|r_{12}^{-1}|IJ\rangle]}{\epsilon_I^{HF} + \epsilon_J^{HF} - \epsilon_A^{HF} - \epsilon_B^{HF}} \tag{3.31}$$

where $Re[x]$ is a function which takes the real part of x. The two-electron integrals in equation (3.31) are infinitesimal numbers [12]. They approach zero when N goes to ∞. To separate the infinitesimal factor, first we introduce the composite index $I = (i, \mathbf{k})$, where i indicates the band and $\mathbf{k}$ the quasi-momentum, which is confined to the first Brillouin zone, and likewise for J, A, and B then using the wave functions given by equation (3.26) we get:

$$\langle IJ|r_{12}^{-1}|AB\rangle = \delta_{\mathbf{k}_j, T(\mathbf{k}_a+\mathbf{k}_b-\mathbf{k}_i)} Q(ijab\mathbf{k}_i\mathbf{k}_a\mathbf{k}_b)/N \tag{3.32}$$

where T($\mathbf{k}$) is a function which shift the vector $\mathbf{k}$ by means of reciprocal lattice vectors back to the first Brillouin zone, and

$$\begin{aligned} Q(ijab\mathbf{k}_i\mathbf{k}_a\mathbf{k}_b) \;=\; & \sum_{\mathbf{R}_j,\mathbf{R}_a,\mathbf{R}_b} exp[i(\mathbf{k}_a\mathbf{R}_a - (\mathbf{k}_a+\mathbf{k}_b-\mathbf{k}_i)\mathbf{R}_j + \mathbf{k}_b\mathbf{R}_b)] \times \\ & \sum_{pqrs} (C_p^{i\mathbf{k}_i})^* (C_r^{jT(\mathbf{k}_a+\mathbf{k}_b-\mathbf{k}_i)})^* C_q^{a\mathbf{k}_a} C_s^{b\mathbf{k}_b} \langle \chi_p \chi_r^{\mathbf{R}_j} | \chi_q^{\mathbf{R}_a} \chi_s^{\mathbf{R}_b} \rangle \end{aligned}$$

has a finite value. By substituting equation (3.32) into equation (3.31) and replacing the summations over the reciprocal vector $\mathbf{k}$ in the first Brillouin zone we get the following expression for the total energy per unit cell:

$$\begin{aligned} E_{uc}^{(2)} = \frac{1}{W_3} \sum_{ijab} \int_{BZ} d\mathbf{k}_i \int_{BZ} d\mathbf{k}_a \int_{BZ} d\mathbf{k}_b \{ & 2|Q(ijab\mathbf{k}_i\mathbf{k}_a\mathbf{k}_b)|^2 \\ & - Re[Q(ijab\mathbf{k}_i\mathbf{k}_a\mathbf{k}_b) Q^*(ijba\mathbf{k}_i\mathbf{k}_b\mathbf{k}_a)]\} \\ & / \epsilon_{i\mathbf{k}_i}^{HF} + \epsilon_{jT(\mathbf{k}_a+\mathbf{k}_b-\mathbf{k}_i)}^{HF} - \epsilon_{a\mathbf{k}_a}^{HF} - \epsilon_{b\mathbf{k}_b}^{HF} \end{aligned}$$

where W_3 is the volume of the first Brillouin zone. However, one of the major advantages of the MP2 in correlation studies is that in this case only matrix elements between the ground state and doubly excited configurations must be computed. The determination of the higher-order correlation corrections will not be an easy task even for medium-sized elementary cells, since also correlations to the wavefunctions have explicitly to be calculated.

3.2.2. Coupled-Cluster Method with Localized Orbitals for Polymers

The coupled-cluster (CC) theory has two main advantages for applications to extended systems like polymers. First of all it is invariant to separate a localization of the occupied and virtual space by unitary transformations and second, it is size extensive, i.e., the results have the proper dependence on the number of electrons. Recently, the use of localized orbitals together with coupled-cluster theory has been implemented for polymers by Förner et al. [22]. In their work they are mainly concerned with localized orbitals obtained by separate unitary transformations in the occupied and virtual subspaces of the HF orbitals, performed CCD and its linear approximation L-CCD calculations for polymers. Here we briefly sketch the method. The theoretical background of CC theory is described in chapter 2, so it is sufficient to give only a brief outline of the CCD ansatz at this point. In CCD the correct wavefunction $|\Psi>$ is written as

$$\Psi = e^{\hat{T}}\Phi_0 \tag{3.33}$$

where Φ_0 is the HF ground state SD and $\hat{T}$ is an excitation operator which is restricted to ($\hat{T} \approx \hat{T}_2$) and thus

$$\Psi = \sum_{\nu=0}^{\infty} \frac{1}{\nu!}\hat{T}_2^{\nu}\Phi_0 \tag{3.34}$$

In the derivation of the CCD equations for the matrix elements T_{JI}^{AB} and for the correlation energy the terms with $\nu > 2$ vanish exactly. The correlation energy is given by

$$E_{corr} = \sum_{IJ}\sum_{AB}\tau \tag{3.35}$$

where

$$\tau = V_{IJ}^{AB}(2T_{IJ}^{AB} - T_{JI}^{AB}) = V_{IJ}^{AB}(\Delta_{IJ}^{AB}) \tag{3.36}$$

$$V_{IJ}^{AB} =< \Phi_I(1)\Phi_J(2)|\frac{1}{r_{12}}|\Phi_A(1)\Phi_B(2) > \tag{3.37}$$

If the necessary matrix elements are computed in localized (WF) basis then the correlation energy per unit cell can be computed directly from them

$$\frac{E_{corr}}{G} = \sum_{e}\sum_{F}\sum_{ST} V_{(e,0)F}^{ST}(WF)\Delta_{(e,0)F}^{ST}(WF) \tag{3.38}$$

In equation (3.38) F, S, T are combined indices $F = (f, q)$, where f is a localized orbital (WF) index and q a cell index. e and f refer to occupied, s and t to virtual WF. $(e, 0)$ denotes the WF e in the reference cell. Introduction of the correlated wave function into Schrödinger equation and projection on the space of double excitations yields the CCD equations for the $\hat{T}_2$ matrix elements

$$T_{IJ}^{RS} =< \Phi_I(1)\Phi_J(2)|\hat{T}_2|\Phi_R(1)\Phi_S(2) > \tag{3.39}$$

$$< \Phi_{IJ}^{RS}|\hat{H}(1 + \hat{T}_2 + \frac{1}{2}\hat{T}_2\hat{T}_2)|\Phi_0 > - < \Phi_{IJ}^{RS}|\hat{T}_2|\Phi_0 > E = 0 \tag{3.40}$$

By defining

$$V_\alpha =< ij|ab >; \qquad T_\alpha = T_{ji}^{ab} =< ij|\hat{T}_2|ab > \tag{3.41}$$

The CCD equations can be written in compact form:

$$\sum_{\beta\beta'} B_{\alpha\beta\beta'} T_\beta T_{\beta'} + \sum_\beta A_{\alpha\beta} T_\beta + V_\alpha = 0 \tag{3.42}$$

If we neglect $\mathbf{B}$ in equation (3.42) the linear approximation (L-CCD) to CCD is obtained. As SCF localized orbitals they applied Boys' [60] orbitals. The further details concerning the evalution of these equations for localized orbitals can be found in ref [61]. However, the method has been applied to calculate total correlation energy per unit cell and correlated correction to the band structure of some polymers. The numerical accuracy of this method and related discussions are presented in references [22, 62, 63, 64]. Therefore we do not go into further details here.

3.2.3. Density Functional Studies of Polymers

One of the most powerful and successful methods in the polymer studies is the density functional theory (DFT), which includes correlation effects in an approximate way, by using a more or less sophisticated exchange-correlation potential. DFT and the local density approximation (LDA) as well as various improvements to the LDA have been briefly described in chapter 2. Therefore, here we will skip the theoretical background of this method and describe how the methods are applied in studies of polymers. However, the DFT methods are developed for polymers especially by Springborg [89]. He and his cowokers have studied various properties of different helical polymers (which are approximated as being periodic in one direction and finite in the other two) and demonstrated how the density functional calculations on polymeric systems can give information of relevance in understanding their electronic and structural properties. Starting point are the single-particle Kohn-Sham [3] equations in which the single-particle eigenfunctions are expanded in a basis of linearized muffin-tin orbitals (LMTOs). The LMTO basis functions are atom-centered orbitals and are defined as follows. The total space is divided into two parts: non-overlapping atom-centered spheres (the so-called muffin-tin

spheres) and the interstitial region. The LMTO centered at the site $\mathbf{R}$ in the interstitial region is defined as

$$h_l^{(1)}(\kappa|\mathbf{r}-\mathbf{R}|)Y_L(\widehat{r-R}) \tag{3.43}$$

where $L=(l,m)$, Y_L is a harmonic function, $(\widehat{r-R})$ a unit vector along $\mathbf{r}-\mathbf{R}$, and κ a purely imaginary decay constant of the spherical Hankel function $h_l^{(1)}$. Inside the muffin-tin sphere, the total effective potential can be expanded in angular components,

$$V(\mathbf{r})=\sum_L \upsilon_{RL}(|\mathbf{r}-\mathbf{R}'|)Y_L(\widehat{r-R'}) \tag{3.44}$$

and by keeping only the spherically symmetic part ($L=(0,0)$), the resulting Kohn-Sham single-particle equations become one-dimensional and can be solved numerically. The LMTOs so defined are eigenfunctions to a muffin-tin potential, i.e. a potential that is spherically symmetric inside the spheres and constant in the interstitial region. By choosing the various parameters well, these functions become reasonably accurate approximations to the exact solutions to the Kohn-Sham equations for the full potential and not only its muffin-tin part. Finally, although the LMTOs are eigenfunctions to a muffin-tin potential it should be stressed that the LMTOs are solely considered as constituting a basis set–the muffin-tin potential is only used in defining the basis functions, whereas the full potential is included in the actual calculations. However, the LMTOs constitute a set of atom-centered basis functions and can therefore be used also for helical polymers. In order to make full use of the helical symmetry one can construct helical Bloch waves from the LMTO.

$$\chi_{j,L,\kappa}^{\mathbf{k}}(\mathbf{r})=\sum_n \chi_{n,j,L,\kappa}(\mathbf{r})e^{i\mathbf{k}n\pi} \tag{3.45}$$

where $\chi_{n,j,L,\kappa}(\mathbf{r})$ is an LMTOs characterized by the decay constant κ in the interstitial region and by the angular dependence given through L, and centered at the jth atom in the nth unit cell. Using the Bloch functions of equation (3.45) it is now possible to calculate the electronic properties of infinite, periodic polymers. The details of how this is done can be found in [65, 66].

3.2.4. Band Structure for Polymers

The orbital energies in extended systems are particular important quantities and they form the so-called band energies or band structure. Band energies of solids can be regarded as energy differences between the N-particle ground state and a state with $N+1$ or $N-1$ particles, respectively, where one delocalized Bloch electron has been added or removed. When a hole is added to the system by removing an electron, it generates a polarization cloud which is moving with it. Also the correlations in the neutral state are modified if a hole is generated. The hole, together with the polarization cloud

surrounding it and the modifications in the ground-state correlations, forms a quasiparticle. At the SCF level, for this kind of process, Koopmans' theorem holds, and the task of determining the band energies can be reduced to finding the one particle energies of the respective Bloch states. Since we have performed band structure calculations for some polymers, now we briefly describe the HF and correlated band structure formalism for polymers. Starting from the HF equation of polymers and solving that equation we have the following Fock matrix elements in the atomic orbital basis:

$$F_{p0,qj} = \langle p(\mathbf{0})|\hat{T} + \hat{U} + \sum_{\beta}(2\hat{J}_{\beta} - \hat{K}_{\beta})|q(\mathbf{R}_j)\rangle \tag{3.46}$$

Since the band structure involves matrix elements of the Fock operator in **k**-space, we transform the orbitals from real to **k**-space:

$$|p(\mathbf{k})\rangle = \frac{1}{\sqrt{N}}\sum_{\mathbf{R}_j} e^{-i\mathbf{k}\mathbf{R}_j}|p(\mathbf{R}_j)\rangle \tag{3.47}$$

The transformation for operators can be written as follows:

$$Q_{pq}(\mathbf{k}) = \sum_{\mathbf{R}_j} e^{-ik\mathbf{R}_j}\langle p(\mathbf{0})|\hat{Q}|q(\mathbf{R}_j)\rangle \tag{3.48}$$

By using $\hat{Q} = \hat{F}$ and $\hat{Q} = 1$ we get the **k**-space Fock and overlap matrix elements, $F_{pq}(\mathbf{k})$ and $S_{pq}(\mathbf{k})$, respectively. Thus, the Hartree-Fock-Roothaan equations in **k**-space can be written as:

$$\sum_{q} F_{pq}(\mathbf{k})C_{q\alpha}(\mathbf{k}) = \epsilon_{\alpha}(\mathbf{k})\sum_{q} S_{pq}(\mathbf{k})C_{q\alpha}(\mathbf{k}) \tag{3.49}$$

Finally, by solving the generalized eigenvalue equations (3.49) one can get the desired quasiparticle energies for a given **k** point. Up to now, the formalism described above does not take into account the effects of correlation on the band structure. The correlated band-structure calculations have been presented recently by Förner et al. [22], based on localized Wannier orbitals employing CC theory. Another approach to correlated band structure calculations which operates entirely in the reciprocal space has been presented by Sun snd Bartlett [21, 67, 68].

However, our calculations has performed employing the HF Wannier orbitals. To this end the theory of effective Hamiltonians [69] was applied, for which we briefly give the main equations. We divide the complete Hilbert space into a finite subspace P of dimension d, called the model space, and its orthogonal complement Q, as indicated by the corresponding projection operators:

$$\hat{P} = \sum_{m=1}^{d} |m><m| \qquad \hat{Q} = \sum_{\alpha} |\alpha><\alpha| \qquad \hat{P} + \hat{Q} = 1 \tag{3.50}$$

A wave operator $\hat{\Omega}$ is constructed to yield d exact solutions Ψ^a of the full Hamiltonian $\hat{H}$ when operating on their projections Ψ_0^a onto the model space P, that means:

$$\Psi^a = \hat{\Omega}\Psi_0^a \tag{3.51}$$

where

$$\Psi_0^a = \hat{P}\Psi^a, \qquad \hat{H}\Psi^a = E^a\Psi^a \tag{3.52}$$

With these quantities an effective Hamiltonian $\hat{H}_{eff}$ is defined to recover the exact eigenenergies when operating on the projected functions Ψ_0^a in the model space according to:

$$\hat{H}_{eff}\Psi_0^a = E^a\Psi_0^a \tag{3.53}$$

This Hamiltonian can be constructed from the wave operator $\hat{\Omega}$ as

$$\hat{H}_{eff} = \hat{P}\hat{H}\hat{\Omega}\hat{P} \tag{3.54}$$

The effective Hamiltonian obeys the generalized Bloch equation

$$[\hat{\Omega}, \hat{H}_0] = (\hat{V}\hat{\Omega} - \hat{\Omega}\hat{P}\hat{V}\hat{\Omega}) \tag{3.55}$$

where the the full Hamiltonian $\hat{H}$ has been partitioned into a zeroth-order Hamiltonian (model Hamiltonian) $\hat{H}_0$ and a perturbation $\hat{V}$. In a perturbative approach, equation (3.55) is calculated order by order, the first three orders being given by

$$[\hat{\Omega}_1, \hat{H}_0]\hat{P} = \hat{Q}\hat{V}\hat{P} \tag{3.56}$$

$$[\hat{\Omega}_2, \hat{H}_0]\hat{P} = \hat{Q}\hat{V}\hat{\Omega}_1\hat{P} - \hat{\Omega}_1\hat{P}\hat{V}\hat{P} \tag{3.57}$$

$$[\hat{\Omega}_3, \hat{H}_0]\hat{P} = \hat{Q}\hat{V}\hat{\Omega}_2\hat{P} - \hat{\Omega}_2\hat{P}\hat{V}\hat{P} - \hat{\Omega}_1\hat{P}\hat{V}\hat{\Omega}_1\hat{P} \tag{3.58}$$

Once the wave operator is calculated, the effective Hamiltonian is given by equation (3.54). Now in order to obtain the desired result, the theory is applied as explained in the following for the case of particles, the hole case being completely equivalent. The HF calculation provides orthonormal and local occupied and virtual orbitals which are denoted by a, b, c and r, s, t respectively. To denote the elements of the effective Hamiltonian, μ and η will be used instead of r, s, t. With the application to periodic systems in mind, each such index comprises a spin index, an orbital index, and a cell index $|\mu >= |\sigma_\mu, o_\mu, \mathbf{R}_\mu >$. From these orbitals, the model space P is constructed to contain the $N+1$-electron determinants $c_r^\dagger|\Psi_{scf} >$ created from the HF ground state $|\Psi_{scf} >$ by adding a particle to the orbital r

$$\hat{P} = \sum_r c_r^\dagger|\Psi_{scf} >< \Psi_{scf}|c_r \tag{3.59}$$

The orthogonal complement Q is approximately given by the single and double excitations applied to the model space, specifically

$$\hat{Q} = \sum_{a,s,r} c_s^\dagger c_a c_r^\dagger|\Psi_{scf} >< \Psi_{scf}|c_r c_a^\dagger c_s + \sum_{a,b,s,t,r} c_t^\dagger c_s^\dagger c_b c_a c_r^\dagger|\Psi_{scf} >< \Psi_{scf}|c_r c_a^\dagger c_b^\dagger c_s c_t \tag{3.60}$$

The entire Hamiltonian $\hat{H}$ is split into the zeroth-order Hamiltonian $\hat{H}_0$ and the perturbation $\hat{V} = \hat{H} - \hat{H}_0$. As zeroth-order Hamiltonian we take the diagonal of the Fock operator $\hat{F}$ in the model space

$$\hat{H}_0 = \sum_r \hat{F}_{rr} \qquad \hat{F}_{rr} =< r|\hat{F}|r > \qquad |r >= c_r^\dagger|\Psi_{scf} > \tag{3.61}$$

and the off-diagonal elements will appear as an additional perturbation with respect to the case of the treatment in CMOs, where $\hat{F}$ is diagonal and $\hat{H}_0 = \hat{F}$. In our applications we calculate the effective Hamiltonian to second order in perturbation theory and include the additional perturbation up to third order. Now the effective Hamiltonian being in general non-hermitian, it is symmetrized by

$$\frac{< \mu|\hat{H}_{eff}|\eta > + < \eta|\hat{H}_{eff}|\mu >}{2} \tag{3.62}$$

To order the excited states, each of them will be associated with a quasi wavenumber k which plays the same role as the wavenumber used in infinite periodic systems. Finally the effective Hamiltonian can be rewritten with explicit indices

$$(\hat{H}_{eff})^{\mathbf{R}}_{\mu,\eta} =< \mu\mathbf{0}|\hat{H}_{eff}|\eta\mathbf{R} > \tag{3.63}$$

where the spin variable σ_μ is taken to be $+\frac{1}{2}$. These matrix elements can be considered as representing a hopping of an electron from orbital μ located in cell $\mathbf{0}$ to an orbital η in cell $\mathbf{R}$. Having obtained the quantity $(\hat{H}_{eff})^{\mathbf{R}}_{\mu,\eta}$ the real space matrix is transformed into the quasi reciprocal space k by virtue of

$$H_{\mu,\eta}(\mathbf{k}) = \sum_{\mathbf{R}} e^{i\mathbf{kR}} < \mathbf{0}\mu|\hat{H}_{eff}|\eta\mathbf{R} > \tag{3.64}$$

Diagonalization in the (quasi) reciprocal space yields the eigenfunctions and eigenenergies, i.e., the band structure.

3.2.5. Incremental Scheme and A Simple Approach

1. Incremental Scheme

The incremental scheme employing localized orbitals has been introduced in wavefunction-based quantum chemical methods and performed on a variety of extended systems: ionic solids, semiconductors and polymers [70, 72, 71, 73]. Here we briefly sketch the general features of this scheme. The incremental scheme is basically an expansion of the total correlation energy per unit cell. If the reference cell in a polymer is labelled by index 0, and the neighboring cells according to their position with respect to the reference cell are denoted by indices $\pm$ 1, $\pm$ 2, etc., one may write the correlation energy per unit cell as a sum of increments

$$E_{corr} = \epsilon_0 + \sum_{i>0} \Delta\epsilon_{0i} + \sum_{j>i>0} \Delta\epsilon_{0ij} + \cdots \tag{3.65}$$

Here $\epsilon_0 = \Delta\epsilon_0$ denotes the correlation energy of the electrons in the reference unit cell and the two-body increments $\Delta\epsilon_{0i}$ are calculated from the correlation energy ϵ_{0i} of the reference cell and the cell at position i by subtracting the one-body terms $\epsilon_0 = \epsilon_i$, i.e.,

$$\Delta\epsilon_{0i} = \epsilon_{0i} - 2 * \epsilon_0 \tag{3.66}$$

Note that, e.g., the increments $\Delta\epsilon_{0i}$ and $\Delta\epsilon_{0,-i}$ are identical and each contributes to both cells 0 and i, respectively $-i$, i.e., the summation can be restricted to positive values of i. The three-body corrections $\Delta\epsilon_{0ij}$ are constructed accordingly, i.e., with $\Delta\epsilon_{0(j-i)} = \Delta\epsilon_{ij}$

$$\Delta\epsilon_{0ij} = \epsilon_{0ij} - 3 * \epsilon_0 - \Delta\epsilon_{0i} - \Delta\epsilon_{0j} - \Delta\epsilon_{0(j-i)} \tag{3.67}$$

Thus, finally summing up all increments, one obtains the exact correlation energy per unit cell of the polymer.
In principle, the exact correlation energy of a system with n bonds is partitioned into a total of $2^n - 1$ increments (symmetry is not exploited) namely the number of possible m-body increments is $\binom{n}{m}$. The procedure described above only makes sence, if the incremental expansion is well convergent and can be truncated at low values m, e.g., after second or third sum. However, the truncation of order of increments and special truncation for a given order is very important. In practical calculation usually the given order of increments is truncated including interactions up to certain nearest neighbor unit cells, e.g., the second sum after the nearest-neighbor (NN) or next-nearest neighbor(NNN) terms. It is known from experience that the contributions from higher-order increments as well as from interactions between more distant cells proved to be negligible.

2. A Simplified Finite-Cluster Approach

In this approach the total energy E_{tot} or correlation energy E_{corr} per unit cell U of a polymer U_∞ can be obtained as the limit

$$E = \lim_{n\to\infty} \frac{E(R(U_n)R')}{n} \tag{3.68}$$

i.e., by performing calculations for increasingly long oligomers $R(U_n)R'$, where the dangling bonds at both ends have been saturated by rest groups R and R', respectively. In order to reduce finite-size effects due to the termination of the oligomers by the rests R and R', one should consider instead

$$E = \lim_{n\to\infty} \triangle E_n = \lim_{n\to\infty} \Big[E(R(U_{n+1})R') - E(R(U_n)R') \Big] \tag{3.69}$$

i.e., the energy changes between two oligomers differing just by a single unit cell. However, the convergence of $\triangle E_n$ with respect to the number of unit cells is much faster for the dynamical correlation energy than for the HF energy, reflecting essentially the local character of electron correlations in contrast to the long-range character of the mean-field interactions. Having at hand HF programs to account accurately for the latter effect (e.g., CRYSTAL, WANNIER), it is tempting to use equation (3.69) only for the correlation energy per unit cell. The choice of the finite cluster will be discussed in the next chapter.

Now we discuss how the simple finite-cluster approach is related to the so-called incremental scheme. However, in finite-cluster calculations the sums in equation (3.68) are terminated, and additional contributions due to the terminal rests R and R' arise. By disregarding the end groups and assuming that the ideal oligomer (starting at cell 0 and ending at cell n) can be considered to be a part of the polymer, one obtains as an approximation to the correlation energy per unit cell E_{corr}

$$E_{corr}(n+1) - E_{corr}(n) = \epsilon_0 + \sum_{i>0}^{n+1} \Delta\epsilon_{0i} + \sum_{j>i>0}^{n+1} \Delta\epsilon_{0ij} + ... + \Delta\epsilon_{012...(n+1)} \tag{3.70}$$

For a convergent incremental expansion the error in the correlation energy per unit cell should be smaller than $\Delta\epsilon_{0n+1}$, which decays as $1/(n+1)^6$ for large n due to van der Waals type correlation contributions. The contributions of the terminal groups R and R' cancel out when building the difference in equation (3.70), except for those terms which refer to one rest and the cell most remote to it in the oligomer, as well as difference in the R-R' two-body increments for oligomers of length $n+1$ and n. Due to the larger distances involved all these corrections should be smaller than $\Delta\epsilon_{0n+1}$, at least as long as the rests bear no net charges. In practical calculations the convergence can be easily checked by comparing results obtained from finite clusters of length $n-1$, n and $n+1$. However, the advantage of the outlined simplified finite-cluster approach is that it can readily be applied to any size-extensive correlation treatment working in canonical orbitals, its disadvantage is that it becomes impracticable for large unit cells or in the 3d case.

4. Applications to Polymers

4.1. Polyiminoborane and Polyaminoborane

The boron–nitrogen polymers polyiminoborane (PIB) $[BNH_2]_\infty$ and polyaminoborane (PAB) $[BNH_4]_\infty$ (figure 4.1) are isoelectronic to polyacetylene (PA) $[C_2H_2]_\infty$ and polyethylene (PE) $[C_2H_4]_\infty$, respectively. For these polymers no experimental information on the structure is available. Previous experimental studies reported cyclic oligoaminoboranes as well as amorphous polyaminoboranes, but the characterization of the polymeric substance still remained incomplete [74]. Recently it was found experimentally for the reaction of $NaBH_4$ with $(NH_4)_2SO_4$ that the formation of PAB is competing with the one of the benzene analogue borazine $B_3N_3H_6$, which is used as a precursor for the technically important synthesis of pure boron nitride via pyrolysis [75]. These systems have been investigated theoretically two decades ago by Armstrong et al. [76], who reported besides semiempirical calculations also the results of ab initio HF partial geometry optimizations, Mulliken population analysis and the band structure for single–zeta basis sets. Furthermore, they obtained a rather large boron–nitrogen bond length alternation of 0.4 Å in case of PAB. On the other hand a possible bond alternation in PIB similar to the one observed in the isoelectronic PA was not investigated.
Here, we have investigated these polymers by applying *ab initio* quantum chemical methods such as the Wannier–orbital–based HF–SCF approach, coupled–cluster (CC) and Møller–Plesset second–order perturbation (MP2) theory. First we have performed geometry optimizations for these systems both at the HF and the correlated level. For each optimized geometry, finally, we calculated the cohesive energy, the polymerization energy and the band structure.

4.1.1. Applied Methods And Technical Details

The recently developed Wannier-orbital-based HF-SCF method, namely the WANNIER code [19], has been applied for the geometry optimization at the HF level. In order to demonstrate the correctness of this method we have also performed Bloch-orbital-based CRYSTAL [17] calculations. Then the structure of each polymer at the correlated level has been optimized with the MOLPRO molecular orbital *ab initio* program package [23] by using the simplified finite–cluster approach outlined last chapter. We have opti-

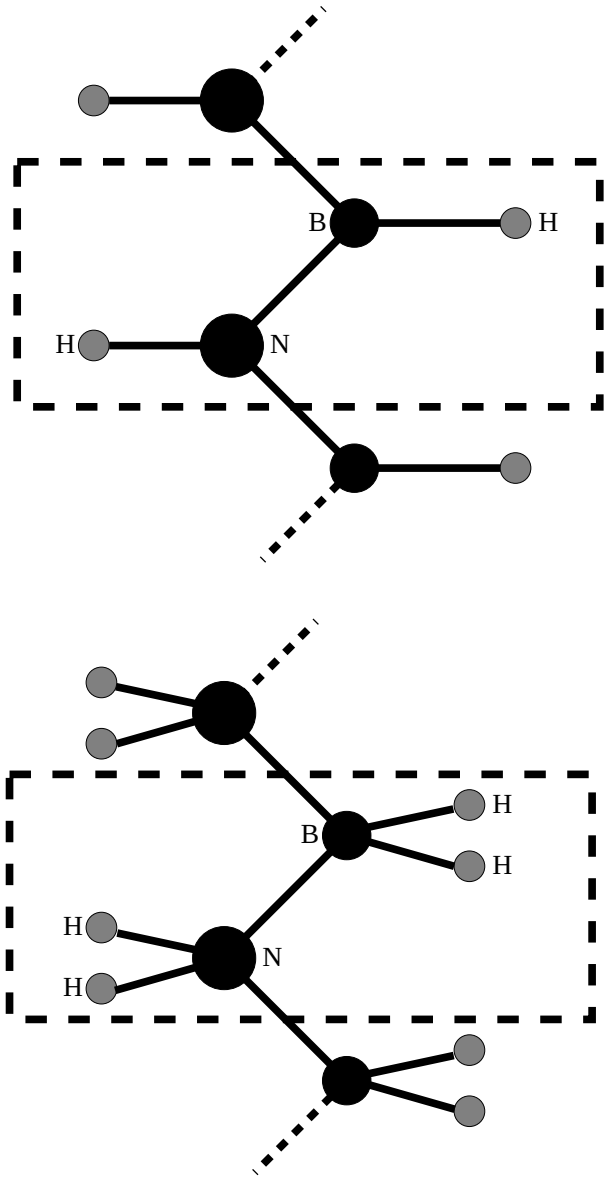

Figure 4.1.: Structures of PIB (top) and PAB (bottom). The unit cell is denoted by dashed boxes.

mized the boron–nitrogen (r_{BN}), boron–hydrogen (r_{BH}) and nitrogen–hydrogen (r_{NH}) bond length, the lattice constant (a), the hydrogen–boron–hydrogen (α) and hydrogen–nitrogen–hydrogen (β) bond angle (in figure 4.1). We adopted polarized valence double–zeta (DZ+P) basis sets, which are also called 6–31G** basis sets. The polarization functions consisted of a single p–type exponent of 0.75 Bohr^{-2} on hydrogen as well as single d–type exponents of 0.6 Bohr^{-2} and 0.8 Bohr^{-2} on boron and nitrogen, respectively. Thus the basis sets are (4s1p)/[2s1p] for hydrogen and (10s4p1d)/[3s2p1d] for boron and nitrogen.
As described in the chapter 2, in the WANNIER program there are two free parameters, namely $\mathcal{N}$, which represents the size of the orthogonality region of the Wannier functions of the reference cell, and M, which represents the range of the Coulomb interaction included in the Fock matrix. In these calculations we have typically chosen $\mathcal{N} = 4$ and $M = 75$ for PIB and $\mathcal{N} = 5$ and $M = 75$ for PAB. The CRYSTAL program uses several computational parameters which determine the accuracy of the Coulomb and the exchange series. The parameter related to the Coulomb series is called ITOL1 and those related to the exchange series are called ITOL3, ITOL4, and ITOL5 [18]. In the current calculation the values of $7, 7, 7$ and 15 are choosen for these parameters and the contributions of all one- and two-electron integrals with absolute values below 10^{-8} a.u. were discarded. To make the comparison with CRYSTAL results transparent, we treated the Coulomb and the exchange series in the WANNIER program with the same accuracy.
Electron correlation contributions were evaluated from finite clusters using a simple approach. The cluster is constructed by putting several unit cells together in which a unit cell in the middle is assumed to be virtually in the same environment as a corresponding unit cell in a polymer of infinite length and the dangling bonds at both ends are saturated by hydrogen atoms. In order to reduce finite-size effects due to the termination of the oligomers we take:

$$E = \lim_{n\to\infty} \triangle E_n = \lim_{n\to\infty} \Big[E(H[BNH_2]_{n+1}H) - E(H[BNH_2]_n H) \Big] \tag{4.1}$$

i.e., the energy changes between two oligomers differing just by a single unit cell. We can write a similar equation for PAB $[BNH_4]_\infty$. Having at hand HF programs to account accurately for the SCF energy (e.g., CRYSTAL, WANNIER) here we use equation (4.1) only for the correlation energy per unit cell. The identical geometrical parameters have to be adopted for the polymer HF and the finite-cluster correlation calculations in each point since the total energy per unit cell is equal to the polymer HF energy plus the finite-cluster correlation energy. In the present calculation for the correlation energies per unit cell, $n = 3$ has been chosen for both systems based upon a study of the convergence of the MP2 correlation energies with cluster size. In order to calculate the cohesive energy (i.e., total energy per unit cell minus the sum of the total energies of the free atoms) per unit cell at the HF and correlated level, the atomic HF–SCF, MP2, CCSD and CCSD(T) reference energies (B : -24.5193 a.u. , -24.5428 a.u. ,

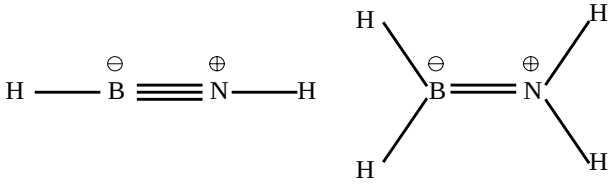

Figure 4.2.: The monomer structures of PIB and PAB.

−24.5613 a.u. and −24.5617 a.u. ; N : −54.3821 a.u. , −54.4149 a.u. , −54.4188 a.u. and −54.4189 a.u. ; H : −0.4982 a.u.) were obtained with the same basis sets as used in the polymer. In addition to the cohesive energy, we have also calculated the polymerization energy (i.e., the total energy per unit cell for the polymer minus the total energy for the corresponding monomer). The structure of the monomer is given in figure (4.2). For monomers BNH_2 and BNH_4 the boron–nitrogen (r_{BN}), boron–hydrogen (r_{BH}) and nitrogen–hydrogen (r_{NH}) bond lengths, nitrogen–boron–hydrogen and boron–nitrogen–hydrogen bond angles were optimized at the SCF and CCSD(T) level employing the MOLPRO program [23]. The applied MP2 and CCSD monomer energies refer to the CCSD(T) equilibrium geometry. The HF band structures of both polymers were computed with the same basis sets using the WANNIER as well as the CRYSTAL program. The correlation correction to the HF band structure was calculated applying the theory of effective Hamiltonians employing the HF WANNIER orbitals. Correlation corrections up to second order of Møller–Plesset perturbation theory were taken into account. The additional perturbation due to the use of localized orbitals was treated up to third order.

4.1.2. Results and Discussion

The results of WANNIER and CRYSTAL HF as well as MP2 and CCSD(T) correlation calculations are summarized in tables (4.1–4.4). As expected, in the tables the ground state HF total energies, cohesive energies and polymerization energies per unit cell as well as the optimized structural parameters demonstrated that the WANNIER results are virtually identical to the CRYSTAL results. One possible reason for slight deviations is the use of Gaussian lobe and cartesian Gaussian functions in WANNIER and CRYSTAL, respectively. From the tables we also see that the MP2, CCSD and CCSD(T) correlation contributions for the structral parameters of PAB and PIB are rather small (table 4.1 and 4.3). Significant changes due to electron correlation however are present in the cohesive energies per unit cell (table 4.2 and 4.4). For PAB the correlation contributions are 6.13 eV, 6.19 eV and 5.40 eV at the MP2, CCSD and CCSD(T) level, respectively. For PIB we obtained 5.14 eV, 4.96 eV and 5.17 eV at the same levels of theory. In both systems electron correlation accounts for 27–28% of the cohesive energy at all three levels of theory.
More relevant for the discussion of the thermodynamic stability of both polymers are

Table 4.1.: Bond lengths (Å) and lattice constant (Å) of polyiminoborane.

Method	r_{BN}	r_{BH}	r_{NH}	a
Finite cluster SCF[b]	1.430	1.195	1.003	2.518
WANNIER SCF	1.429	1.194	1.000	2.517
CRYSTAL SCF	1.428	1.194	1.000	2.513
Finite cluster MP2[b]	1.439	1.201	1.020	2.528
MP2[a]	1.436	1.195	1.025	2.522
CCSD[a]	1.436	1.195	1.029	2.524
CCSD(T)[a]	1.438	1.194	1.010	2.526

[a] optimized value with respect to WANNIER SCF data.
[b] n=4 in equation (4.1).

Table 4.2.: Total energy E_{tot} (Hartree), cohesive energy $\triangle E_{coh}$ (eV), and polymerization energy $\triangle E_{pol}$ (eV) per unit BNH_2 of polyiminoborane.

Method	E_{tot}	$\triangle E_{coh}$	$\triangle E_{pol}$
Finite cluster SCF[b]	-80.3865	13.30	2.45
WANNIER SCF	-80.3866	13.30	2.45
CRYSTAL SCF	-80.3864	13.29	2.44
Finite cluster MP2[b]	-80.6316	18.44	2.32
MP2[a]	-80.6316	18.44	2.32
CCSD[a]	-80.6476	18.26	2.33
CCSD(T)[a]	-80.6559	18.47	2.30

[a] correlation contributions added to WANNIER SCF energies.
[b] as table (4.1)

Table 4.3.: Bond lengths (Å), lattice constant (Å), and bond angles (°) of polyaminoborane.

Method	r_{BN}	r_{BH}	r_{NH}	a	α	β
Finite cluster SCF[b]	1.611	1.198	1.006	2.635	115.6	106.4
WANNIER SCF	1.606	1.198	1.006	2.634	115.6	106.6
CRYSTAL SCF	1.605	1.197	1.006	2.632	115.7	106.7
Finite cluster MP2[b]	1.607	1.200	1.022	2.631	116.2[b]	106.5[b]
MP2[a]	1.601	1.199	1.019	2.625	115.7	105.7
CCSD[a]	1.604	1.201	1.019	2.629	115.4	105.7
CCSD(T)[a]	1.605	1.202	1.019	2.629	115.4	105.7

[a] optimized value with respect to WANNIER SCF data.
[b] n=4 in equation (4.1).

Table 4.4.: Total energy E_{tot} (Hartree), cohesive energy $\triangle E_{coh}$ (eV), and polymerization energy $\triangle E_{pol}$ (eV) per unit BNH_4 of polyaminoborane.

Method	E_{tot}	$\triangle E_{coh}$	$\triangle E_{pol}$
Finite cluster SCF[b]	-81.5026	16.55	0.11
WANNIER SCF	-81.5056	16.63	0.19
CRYSTAL SCF	-81.5055	16.63	0.20
Finite cluster MP2[b]	-81.7841	20.68	0.54
MP2[a]	-81.7870	22.76	0.62
CCSD[a]	-81.8116	22.82	0.54
CCSD(T)[a]	-81.8200	22.03	0.58

[a] correlation contributions added to WANNIER SCF energies.
[b] as table (4.3)

Table 4.5.: The SCF total energy and MP2 correlation energy (in a.u.) convergence with respect to the cluster size n.

	PIB		PAB	
ΔE_n	E_{SCF}	E_{Corr}	E_{SCF}	E_{Corr}
$4-3$	-80.38585160	-0.24568818	-81.50042770	-0.28180725
$5-4$	-80.38587959	-0.24574039	-81.50222047	-0.28181691
$6-5$	-80.38588431	-0.24574849	-81.50320099	-0.28183363
$7-6$	-80.38588450	-0.24575407	-81.50377987	$*****$

the energies of polymerization per unit cell (table 4.2 and 4.4). PIB appears to be fairly stable with respect to the monomer iminoborane BNH_2 ($\triangle E_{pol} \sim 2.3\ eV$), whereas PAB is only weakly bound against its monomer aminoborane BNH_4 ($\triangle E_{pol} \sim 0.6\ eV$). The stability of the polymers with respect to small oligomer ring systems was also investigated. Borazine $B_3N_3H_6$ is isoelectronic to benzene C_6H_6 and was calculated to be 0.01 eV per BNH_2 unit more stable than PIB at the SCF level, but 1.00 eV less stable at the MP2 level. PAB was calculated to be more stable than cyclo–di– and cyclo–triaminoborane $B_nN_nH_{4n}$ (n= 2, 3) by 0.07 eV and 0.08 eV, respectively, at the SCF level. The corresponding MP2 values are 0.92 eV and 0.87 eV. All results reported here refer to the fully optimized geometries of the polymers, oligomers and monomers, both at the SCF and MP2 level.

However, in these calculations the correlation energies per unit cell have been derived from the difference E($B_4N_4H_{10}$) - E($B_3N_3H_8$) for PIB, and from the difference E($B_4N_4H_{18}$) - E($B_3N_3H_{14}$) for PAB. Based upon a comparison with E($B_5N_5H_{12}$) - E($B_4N_4H_{10}$) and E($B_5N_5H_{22}$) - E($B_4N_4H_{18}$) we estimate the convergence of the MP2 correlation contributions to be better than 0.05 mH (milli–Hartree $= 10^{-3}$ a.u.) and 0.01 mH for PIB and PAB, respectively. In case of the SCF energy we achieve convergence to 0.03 mH for PIB, but only to 1.79 mH for the more ionic PAB. In addition, the further convergence behaviour of HF and MP2 correlation energies with respect to the cluster size are also summarized in table (4.5). As it is shown in the table, the HF data for the simple finite cluster approach shows quite good agreement for PIB, whereas in case of PAB some discrepancies due to the slow convergence of $\triangle E_n$ in equation (4.1) with respect to n are obvious. However, in the case of PAB, we did not obtain results for the larger cluster $B_7N_7H_{30}$ at the correlated level since nowadays, the standard MOLPRO program can handle at most around 100 electrons at the correlated level with large basis sets. Therefore our calculation has also some limitations.

In the case of band structures of these polymers, for the boundaries $\Gamma(k = 0)$ and $X(k = \frac{\pi}{a})$ of the Brillouin zone the energy values of the upper three valence bands (v_1-v_3) and the lower two conduction bands (c_1, c_2) around the Fermi level both at the HF

Table 4.6.: Both the HF results (in a.u.) as well as the second–order Møller–Plesset correlation correction results (in a.u.) with third–order localization diagrams included ($MP2(3)$) are given for the upper three valence bands (v_1-v_3) and the lower two conduction bands (c_1, c_2) at the Γ point as well as the X point ($\frac{\pi}{a}$) for polyiminoborane.

	PIB			
	Γ		X	
	HF	$MP2(3)$	HF	$MP2(3)$
v_1	-0.513	-0.452	-0.656	-0.543
v_2	-0.503	-0.369	-0.485	-0.419
v_3	-0.486	-0.338	-0.365	-0.200
c_1	0.205	0.120	0.149	0.050
c_2	0.238	0.146	0.311	0.239
gap			0.514	0.250

and correlated level are presented in table (4.6-4.7). The fundamental band gap is also stated. From the table one can see quantitatively that the electron correlation effect tends to reduce the fundamental band gap in both polymers.

Finally it should be noted that PIB and PAB have previously been investigated at the HF level using single–zeta basis sets and imposing a nearest–neighbour approximation for the interaction between unit cells by Armstrong et al. [76]. Due to the better quality of the basis set used in the present work, i.e., valence double–zeta plus polarization, a quantitative comparison is not possible. However, an important qualitative result obtained by Armstrong et al. is the large boron–nitrogen bond alternation of 0.4 Å for PAB, which is not found in the present work. One possible reason might be the nearest–neighbour approximation adopted by Armstrong et al.. If we use equation (4.1) at the HF level for n=3, we obtain a bond alternation of about 0.03 Å, which is slightly diminished by including electron correlation at the MP2 level and appears to vanish for $n \to \infty$. This is shown in figure (4.3). We note that the averaged boron–nitrogen bond length is very stable even for small cluster sizes. According to our results PAB does not consist of complexed BH_2NH_2 monomer units, i.e., alternating dative nitrogen→ boron and covalent nitrogen–boron σ bonds characterizing a "coordination polymer", but rather contains non–alternating polar covalent nitrogen–boron σ bonds. In the case of PIB, due to the high electronegativity difference between boron and nitrogen the free electron pair remains localized on nitrogen rather than forming a dative nitrogen → boron π bond, i.e. alternation of single and double bonds is not observed , but again a small bond alternation of 0.003 Å is observed when the finite–cluster approach with

Table 4.7.: As table (4.6), but for polyaminoborane.

	PAB			
	Γ		X	
	HF	$MP2(3)$	HF	$MP2(3)$
v_1	−0.463	−0.408	−0.623	−0.520
v_2	−0.456	−0.351	−0.469	−0.431
v_3	−0.433	−0.262	−0.405	−0.276
c_1	0.155	0.090	0.265	0.179
c_2	0.216	0.161	0.350	0.287
gap	0.588	0.352		

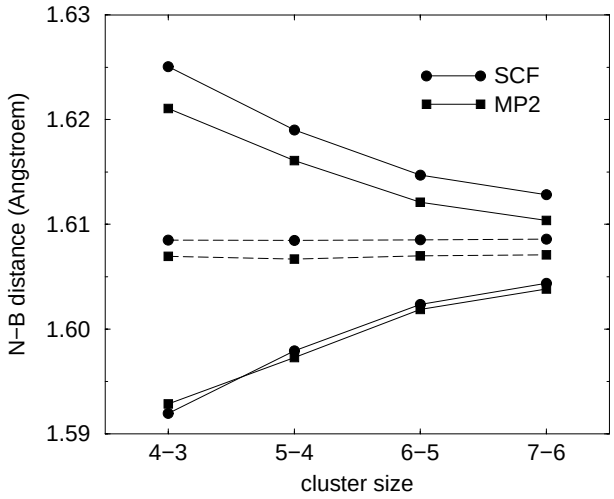

Figure 4.3.: Convergence of the boron–nitrogen bond length in PAB for finite cluster calculations using equation (4.1). The numbers n on the horizontal axis denote that the energy per unit cell was derived as the difference between energies of two oligomers with $n+1$ and n unit cells. Solid lines refer to the individual alternating boron–nitrogen bond lengths, dashed lines to their average.

n=3 in equation (4.1) is adopted. Furthermore, if we look at the density along the B–N chain in small oligomer models $B_4N_4H_{10}$ of PIB and $B_4N_4H_{18}$ of PAB (figure 4.4), the density is still periodic and the B–N bonds are not equivalent. On the other hand, even for small oligomer models of PIB the underlying finite–size effects do virtually not affect the σ–electron system (density in the molecular plane along the B–N chain, figure 4.4a), but they have a noticeable effect on the easily polarizable π–electron system (density 1 a.u. above the molecular plane along the projected B–N chain, figure 4.4b). The HF band structures for PIB and PAB are plotted in figure (4.5). The agreement between the WANNIER HF band structure and the one obtained with the CRYSTAL program is very good. However, the small differences between the two plots are mainly due to the different basis function types. Clearly, the band structures obtained from the two approaches are in excellent agreement for the occupied bands and for the lowest conduction bands. The values of the band gap (at k= π/a point) 0.5141 a.u. (13.99 eV) and 0.6700 a.u. (18.23 eV) obtained with WANNIER agree well with the corresponding CRYSTAL values of 0.5126 a.u. (13.95 eV) and 0.6718 a.u. (18.28 eV) for PIB and PAB, respectively. Qualitatively our band structures agree also with those obtained by Armstrong et al., however, quantitatively we observe some differences which are most likely due to the poorer basis sets used by these authors. In addition we obtained correlation corrections to the HF band structure as mentioned above. They are displayed in figure (4.6) as dashed lines, both for PIB and PAB. For the sake of comparison the HF bands are also displayed in the same viewgraphs as solid lines. In both cases an overall flattening of the bands as well as the closing of the gap (40% and 51% for PAB and PIB, respectively, cf. table 4.6 and 4.7) is clearly visible by virtue of comparison with the HF bands. These two effects are typical of band structure correlation corrections.

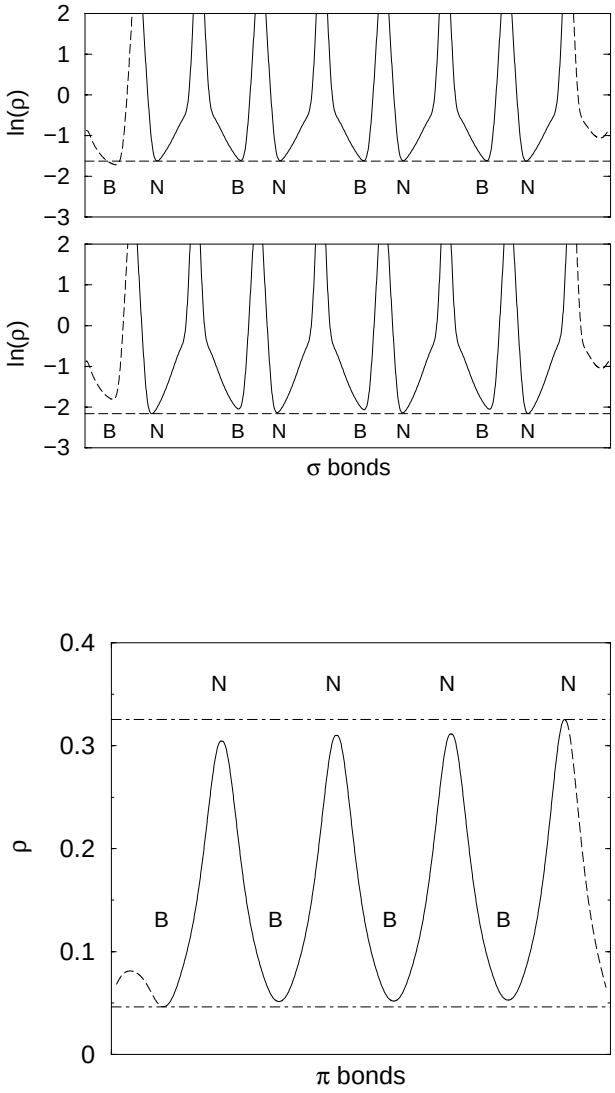

Figure 4.4.: Density along the B–N chain in $B_4N_4H_{10}$ (a, top) and $B_4N_4H_{18}$ (a, bottom) and density along the projection of this chain onto a parallel plane 1 a.u. above the $B_4N_4H_{10}$ molecular plane (b).

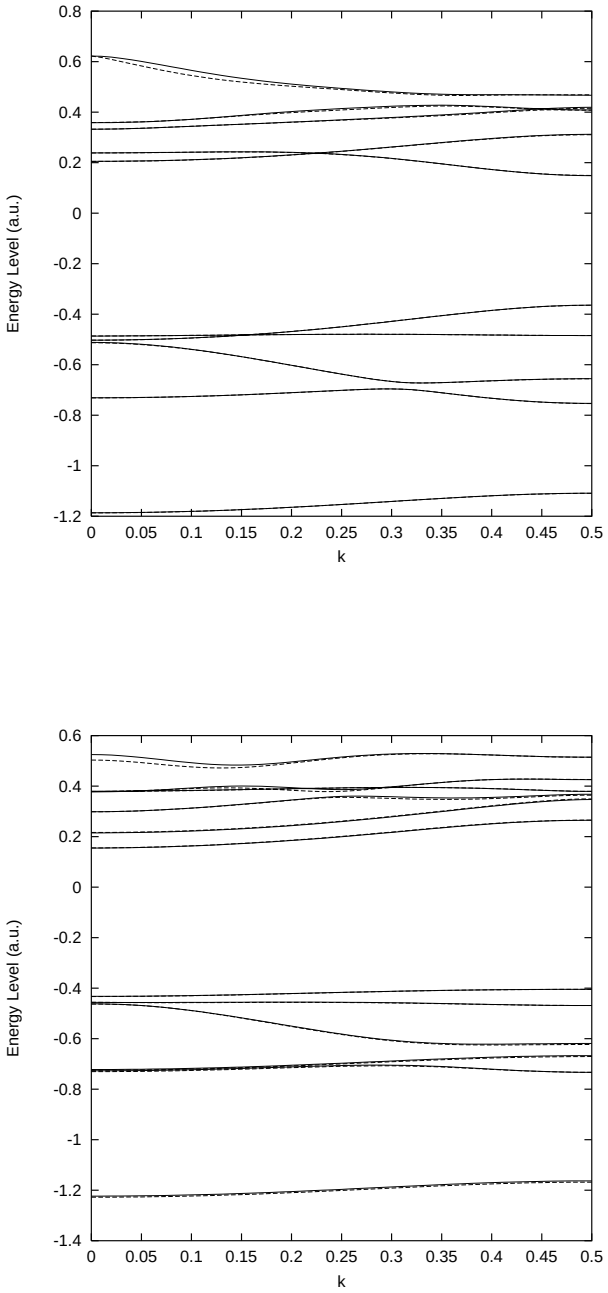

Figure 4.5.: Band structures of PIB (a) and PAB (b) obtained using the WANNIER (solid lines) and CRYSTAL (dashed lines) program packages. The optimized geometry and 6–31G^{**} basis sets were used in both cases. Values of k (horizontal axis) are expressed in units of π/a.

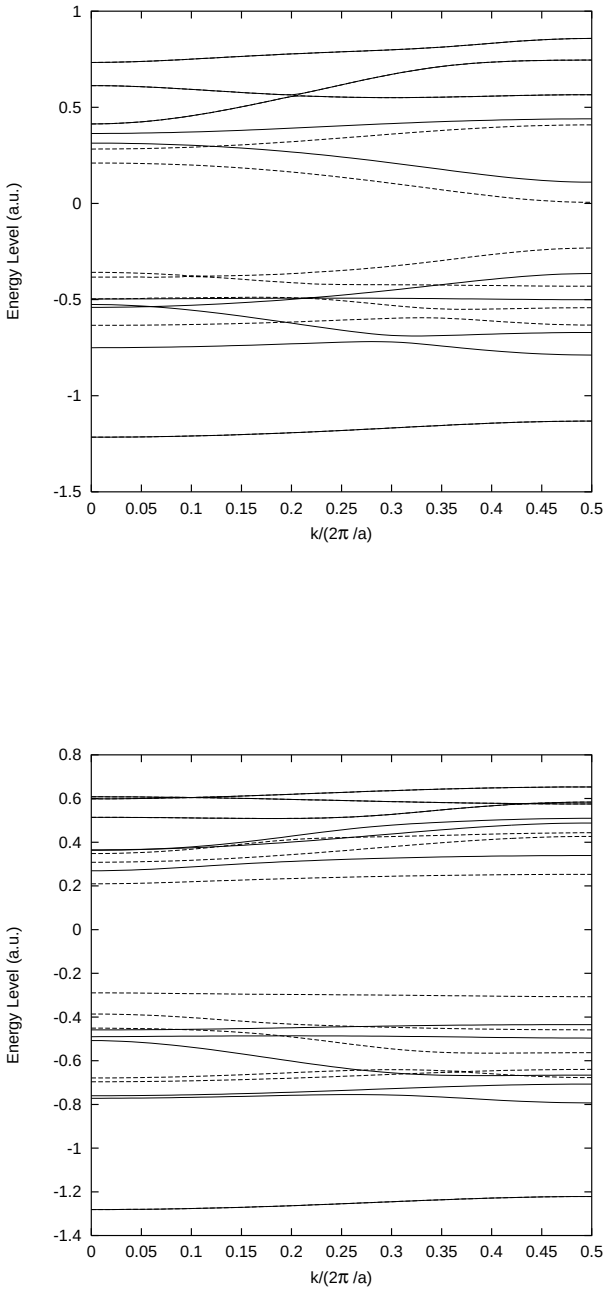

Figure 4.6.: Correlation corrected band structures of PIB (a) and PAB (b) obtained from second–order perturbation theory (dashed lines) in comparison to uncorrelated Hartree–Fock results (solid lines).

4.1.3. Conclusion

We have applied the recently developed Wannier-function-based HF approach to determine the equilibrium structures of one-dimensional periodic systems, i.e., PIB and PAB. Our results have demonstrated the equivalence of this method to the usual approaches based on (delocalized) Bloch orbitals. The localized Wannier orbitals are specially suitable for a subsequent treatment of electron correlation effects using standard quantum chemical methods by means of the so-called incremental scheme. The correlation contributions for the structural parameters of PIB and PAB are rather small. We have calculated the total energy, the cohesive energy and the polymerization energyn per unit cell both at the HF and the correlated level. In both systems electron correlations accounts for $27\% - 28\%$ of the cohesive energy at all three levels of theory. In addition we obtained the HF and correlation-corrected band structure. The correlation effects lead to a decrease of the fundamental gap of PIB and PAB by 40% and 51%, respectively. In particular, in contrast to previous authors, PAB is found to be a weekly bounded covalent polymer without boron-nitrogen bond alternation.

4.2. Lithium Hydride Chain and Beryllium Hydride Polymer

The lithium hydride chain $[LiH]_\infty$ and the beryllium hydride $[Be_2H_4]_\infty$ polymer were studied by applying different quantum chemical methods. For the model system $[LiH]_\infty$, the correlation effects were computed by considering virtual excitations from the occupied Hartree-Fock Wannier functions of the infinite chain into the complementary space of localized unoccupied orbitals, employing a full-configuration-interaction scheme. However, the FCI method based on polymer Wannier orbitals can at present be used only for systems with a less complicated unit cell. Therefore, for beryllium hydride $[Be_2H_4]_\infty$ polymer, the electron correlation contributions to its ground state energy were calculated by considering finite clusters employing a simple approach. Methods such as Møller–Plesset second–order perturbation theory and coupled–cluster singles, doubles and triples level of theory were employed. We have calculated the equilibrium geometry, the cohesive energy and the polymerization energy per unit cell for both polymers.

4.2.1. Lithium Hydride Chain $[(LiH)_\infty]$

Recently, the Wannier-function-based approach has extended to include electron correlation effects using a combination of the full configuration interaction (FCI) method and the so-called incremental scheme [14, 15, 16]. Its application to the three-dimensional lithium hydride solid has been presented [58]. Here we applied it to the model polymers lithium hydride chain $[LiH]_\infty$.
Accurate the HF ground state calculations are a necessary prerequisite for the application of the incremental approach to electron correlation. We performed such calculations for a lithium hydride chain oriented along the x-axis using the WANNIER code [19]. The reference cell contained hydrogen at the (0,0,0) and lithium at the $(a/2, 0, 0)$ position, where a is the lattice constant. We adopted the extended basis set optimized by Dovesi *et al.* [77] which is (7s1p)/[3s1p] for H and (7s1p)/[2s1p] for Li. The total HF energy per unit cell for various lattice constants near the equilibrium was fitted to a cubic polynomial in order to derive the ground state HF equilibrium lattice constant and the total energy per unit cell. After determining the Wannier orbitals for each value of the lattice constant, the corresponding FCI calculations were performed by means of the incremental scheme in which the correlation energy per unit cell is expanded as

$$E_{corr} = \sum_i \varepsilon_i + \sum_{<ij>} \Delta\varepsilon_{ij} + \sum_{<ijk>} \Delta\varepsilon_{ijk} + ... \tag{4.2}$$

Here the summation over i involves Wannier functions located the reference cell, while those over j and k include all the Wannier functions of the crystal. The "one–body" increments $\varepsilon_i = \Delta\varepsilon_i$ are computed by considering virtual excitations only from the i-th Wannier function, freezing the rest of the polymer at the HF level. The "two–body"

increments $\Delta\varepsilon_{ij}$ are defined as $\Delta\varepsilon_{ij} = \varepsilon_{ij} - (\Delta\varepsilon_i + \Delta\varepsilon_j)$ where ε_{ij} is the correlation energy of the system obtained by correlating two distinct Wannier functions i and j. Thus $\Delta\varepsilon_{ij}$ represents the correlation contribution of electrons localized on two "bodies" i and j. Here, the expansion of the correlation energy per unit cell was restricted to one– and two–body increments, and included interactions up to third–nearest neighbor unit cells. Contributions from higher order increments as well as from interactions between more distant cells proved to be negligible. However, when we calculate the correlation contributions via equation (4.2), except for the orbitals involved (say orbitals i and j for the two-body increment $\Delta\epsilon_{ij}$), the rest of the occupied Wannier orbitals are held frozen at the HF level. The region containing these frozen orbitals plays the role of the "environment" for the electrons involved in the correlated calculations, and its contribution can be absorbed in the so-called "environment potential" U^{env} defined as

$$U_{pq}^{\mathrm{env}} = \sum_{\alpha(\mathbf{R}_j)\in\mathcal{E}} (2\langle p\alpha(\mathbf{R}_j)|\frac{1}{r_{12}}|q\alpha(\mathbf{R}_j)\rangle - \langle p\alpha(\mathbf{R}_j)|\frac{1}{r_{12}}|\alpha(\mathbf{R}_j)q\rangle) \,, \tag{4.3}$$

where $\mathcal{E}$ represents the unit cells of the environment, p and q are two arbitrary basis functions, and the factor of two in the first term is due to the spin summation. The sum of equation (4.3) involves an infinite lattice sum over the environment unit cells, and is computed by simply subtracting from the lattice summed J and K integrals obtained at the end of the HF iterations, the contributions corresponding to the orbitals being correlated. Once U_{pq}^{env} has been computed, one is left with an effective Hamiltonian involving a finite number of electrons located in the region whose Wannier orbitals are being correlated. Physically speaking U_{pq}^{env} represents the influence of the environment electrons on the electrons being correlated, explicitly. In these calculations the Li $1s^2$ core shell was also kept frozen, and its contribution was also included in U_{pq}^{env}. The basis functions p and q were restricted to those of the reference cell and the adjacent cells up to the third-nearest neighbors. The virtual orbitals used for computing the correlation effects were also localized. The number of virtual orbitals per unit cell considered for a specific increment corresponds to the number of basis functions per unit cell minus the number of occupied orbitals per unit cell. The virtual orbitals have been expanded in the same basis set as described above for U_{pq}^{env}. The equilibrium values for the FCI energy per unit cell and the lattice constant were determined as described for the HF results. The main contribution of 98.8 % to the correlation energy per unit cell at the equilibrium geometry (E=$-0.0307a.u.$) comes from the one-body term. Two-body terms for first–, second– and third–nearest neighbors contribute with 1.15, 0.01 and 0.001 %, respectively. Obtained results are summarized in table (4.8). It is quite obvious from table (4.8) that, as a function of distance, the two-body correlation effects converge very rapidly. Since the Li basis set used here is suitable only for the ionic LiH molecule, we cannot get a good result for the atomic reference energy of the neutral Li atom (which is needed to determine the cohesive energy). Therefore, for this almost ideally ionic chain the cohesive energies both at the HF and the correlated level are obtained by subtracting the electron

Table 4.8.: Various increments to the correlation energy (Hartree) computed by the Wannier-function-based approach presented in this work. The results refer to a lattice constant of 3.30 Å. NN stands for nearest neighbors.

Correlation Increment	Energy
one-body	-0.0303345
two-body (1NN)	-0.0003538
two-body (2NN)	-0.0000035
two-body (3NN)	-0.0000003

Table 4.9.: Total energy E_{tot} (Hartree), cohesive energy $\triangle E_{coh}$ (eV), polymerization energy $\triangle E_{pol}$ (eV) per unit cell and lattice constant a (Å) of the lithium hydride chain.

Method	E_{tot}	$\triangle E_{coh}$	$\triangle E_{pol}$	a
WANNIER SCF	-8.038047	3.8760	1.8067	3.3273
CRYSTAL SCF	-8.038031	3.8759	1.8063	3.3274
FCI	-8.068744	4.6545	1.4854	3.3300

affinities (EA) and the ionization potential (IP) from the dissociation energy calculated with respect to the ions Li^+ and H^-. The HF values of EA and IP are determined using the finite–difference atomic HF program MCHF [78]. The experimental values of EA and IP were taken as the CI limit, i.e., disregarding the very small relativistic effects. For the polymerization energy we optimized the Li–H distance for the $^1\Sigma^+$ ground state of the monomer at the HF and CI level. Our results are summarized in table (4.9). It is clear from table (4.9) that, correlation effects contribute significantly to the cohesive energy. However, they do not make any significant contribution to the lattice constant of the system.

4.2.2. Beryllium Hydride Polymer $[(Be_2H_4)_\infty]$

Beryllium hydride has attracted considerable interest as a rocket fuel on account of its high heat of combustion. It has also been considered as a moderator for nuclear reactors. It is also known from previous studies [79] that it is poisonous and difficult to prepare experimentally. However, even though there is no or very little experimental information about the structure, the polymer has been studied theoretically using reliable *ab initio* methods at the HF level by Karpfen [80]. Here we have studied this polymer at the HF and the correlated level. The structure of this polymer as shown in figure (4.7) the

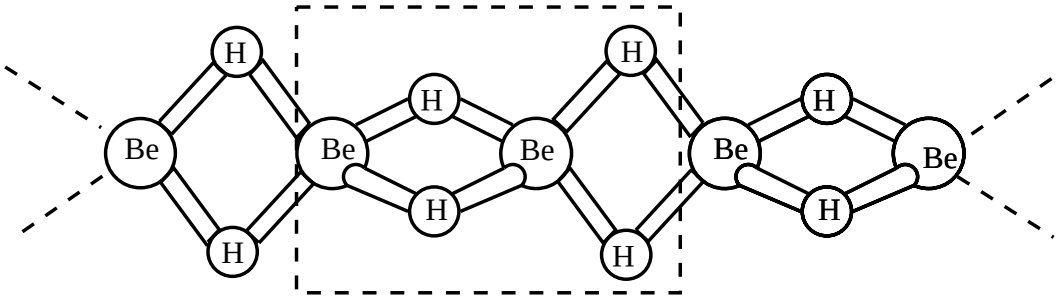

Figure 4.7.: The structure of beryllium hydride polymer. The unit cell is denoted by dashed boxes.

unit cell included two beryllium and four hydrogen atoms and has a perfect tetrahedral structure with all four Be-H bond distances equal. We have optimized the beryllium–hydride bond length (r_{BeH}) and the lattice constant (a). We adopted (DZ+P) basis sets, namely (10s4p1d)/(3s2p1d) for beryllium and (4s1p)/(2s1p) for hydrogen. The polarization functions consisted of a single p–type exponent of 0.75 Bohr^{-2} on hydrogen and a single d–type exponents of 0.4 Bohr^{-2} on beryllium. First we optimized the structure at the HF–SCF level using the CRYSTAL [17] program in which for the basis set we optimized the most diffuse s–type exponent, which is less than 0.1 in the original 6–31G** basis set, and obtained 0.15. A smaller value causes linear dependencies in the basis set when applied in the infinite system.
The correlation energy contributions at each geometry have been calculated with the MOLPRO molecular orbital *ab initio* program package [23] at the MP2, CCSD (CC singles and doubles) and CCSD(T) (CCSD with a perturbative estimate of triples) level by using the simplified finite–cluster approach in which the total energy E_{tot} per $[Be_2H_4]$ unit cell of beryllium hydride is obtained by considering

$$E = \lim_{n\to\infty} \triangle E_n = \lim_{n\to\infty} \Big[E(Be_{2n+3}H_{4n+6}) - E(Be_{2n+1}H_{4n+2}) \Big] \tag{4.4}$$

i.e., the energy change between subsequent oligomers differing by a single unit cell. In our calculations we chose $n = 3$, since the correlation energy converges rapidly with respect to the cluster size, i.e., for n=3, one finds $\triangle E_4 - \triangle E_3 \approx 10^{-6}$ a.u.. We have also calculated the cohesive energy per unit cell at the HF and the correlated level. The atomic HF–SCF, MP2, CCSD and CCSD(T) reference energies (Be: -14.5668 a.u., -14.5928 a.u., -14.6131 a.u. and -14.6131 a.u.; H: -0.4982 a.u.) were obtained with the original 6–31G** basis sets. In addition to the cohesive energy, we have also calculated the polymerization energy. The monomer structure is chosen to be linear (the bond angle is 180Å) the beryllium-hydrogen (Be-H) distance was optimized at the SCF, MP2, CCSD, and CCSD(T) levels of theory (results are summarized in table (4.10)) employing the MOLPRO program [23]. Then the obtained monomer energy is multiplied by two in order to get the correct polymerization energy for polymers. Our

Table 4.10.: Total energy E_{tot} (Hartree) and Be–H distance h (Å) of beryllium hydride monomer.

	SCF	MP2	CCSD	CCSD(T)
h	1.3396	1.3367	1.3376	1.3379
total energy	-15.7664	-15.8171	-15.8329	-15.8333

Table 4.11.: Total energy E_{tot} (Hartree), cohesive energy $\triangle E_{coh}$ (eV), polymerization energy $\triangle E_{pol}$ (eV) per unit Be_2H_4 and lattice constant a (Å), Be–H distance h ($\mathring{A}$) of beryllium hydride polymer.

Method	E_{tot}	$\triangle E_{coh}$	$\triangle E_{pol}$	a	h
CRYSTAL SCF	-31.6300	13.70	2.645	3.958	1.467
MP2[a]	-31.7608	15.85	3.445	3.919	1.456
CCSD[a]	-31.7908	15.56	3.402	3.922	1.457
CCSD(T)[a]	-31.7944	15.66	3.478	3.922	1.458
Karpfen[b]	-31.5780	–	–	4.024	1.470

[a] correlation contributions added to CRYSTAL SCF energies.
[b] See Ref. [80].

final results are summarized in table (4.11). Due to the absence of experimental data or theoretical results at the correlated level, we compare our results only at the HF level to the results of Karpfen [80]. This author has performed a geometry optimization for this polymer with $7, 1/4$ basis sets considering third neighbor's interactions within an ab initio crystal Hartree–Fock approach and his results are also given in table (4.11). Our beryllium–hydrogen bond length is in good agreement with the one obtained by Karpfen, but our HF energy is lower by 0.05 a.u.. A possible reason is the use of d functions in our basis sets.

4.2.3. Conclusion

In conclusion, given a well-localized basis set of Wannier orbitals size-extensive standard quantum chemical methods such as the full configuration interaction method, coupled-cluster or many-body perturbation theory can be applied to evaluate ground state properties of polymers. Here, the full configuration interaction method has been applied to the simple model of the lithium hydride chain by means of the incremental scheme and rapid convergence of the incremental expansion of the correlation energy is obtained. From the results we can see that the correlation effects contribute significantly to the

cohesive energy but do not make any significant contribution to the lattice constant. In the beryllium hydride polymer electron correlation accounts for 12–14% of the cohesive energy and 22–24% of the polymerization energy at all three levels of theory and reduces the lattice constant.

4.3. Polymethineimine

Atomic nitrogen is isoelectronic with CH, and the replacement of every second CH by N in polyacetylene (PA) $[C_2H_2]_\infty$ leads to polymethineimine (PMI). It was first synthesized in the early seventies by Wöhrle [81] and conductivity measurements indicated that the system is a semiconductor [82]. The presence of a $C = N$ double bond the bond alternation along the chain has been experimentally confirmed [82]. Theoretically the PMI system has been investigated at different levels of theory since there is no experimental information about the structure. The first *ab initio* Hartree-Fock (HF) self-consistent field (SCF) study of *all-trans* PMI by Karpfen [83] 1979 already confirmed the experimentally observed bond alternation. Geometry optimizations [83, 84, 85] and a normal mode vibrational frequency analysis have been carried out at the HF [85] and more recently at the second-order many-body perturbation theory (MBPT(2)) [84] levels. Corresponding density functional theory (DFT) results have also been published [86]. Valence effective Hamiltonian (VEH) [87], *ab initio* HF [83, 88], MBPT(2) [84], and linear muffin-tin orbital (LMTO) DFT [89] band structures were also obtained. The frequency-dependent polarizability was studied within coupled-HF theory at the double-zeta basis set level by Gu et al. [90]. Finally, a theoretical investigation of polaron-type defects on the electronic properties has been presented by Del Nero et al. [91]. Here the different structure and thermodynamic stability of *all-trans* PMI in its ground state is investigated by applying *ab initio* HF, MBPT(2) and CC (coupled-cluster) theory. The unit cell structure is shown in figure (4.8). Furthermore, the stability of PMI with respect to its monomer hydrogen cyanide HCN and the small cyclic oligomer 1,3,5-triazine $C_3N_3H_3$ are also discussed.

4.3.1. Applied Methods and Computational Details.

A wave-function-based *ab initio* approach has applied to explore the electronic ground-state properties of the isolated infinite periodic chain. We adopted standard polarized valence double-zeta (6-31G**) basis sets. The polarization functions consisted of a single p-type exponent of 0.75 Bohr^{-2} on hydrogen and single d-type exponents of 0.6 Bohr^{-2} and 0.8 Bohr^{-2} on carbon and nitrogen, respectively. Thus the basis sets are (4s1p)/[2s1p] for hydrogen and (10s4p1d)/[3s2p1d] for carbon and nitrogen. Assuming all C-N bonds to have the same lengths and the C-H bonds to be perpendicular to the polymer axis, first we optimized the equidistant structure of *all-trans* PMI at the HF-SCF level using the WANNIER [19] program. In order to be demonstrate the

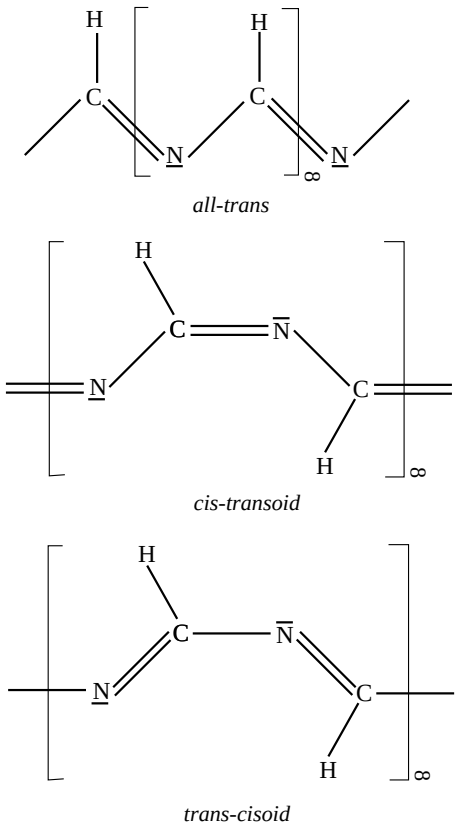

Figure 4.8.: The different structures of PMI.

correctness of the Wannier-orbital-based method, the structure has also been optimized by using the Bloch-orbital-based CRYSTAL [17] program. Since basis sets expanded in Gaussian lobe functions and Cartesian Gaussian functions are used in these programs, the derived results are very similar, but not identical. Then the correlation energy contributions at each geometry have been calculated with the MOLPRO molecular orbital *ab initio* program package at the MP2, CCSD (CC singles and doubles) and CCSD(T) (CCSD with a perturbative estimate of triples) levels from finite clusters applying a simple approach. Although the CCSD(T) approach is one of the most successful and accurate single-reference based methods, nevertheless we include CCSD and MP2 for the purpose of discussion and for comparision to work of other authors. The obtained optimized geometry at the CCSD(T) level is then taken as starting point for the geometry optimization of the alternant structure. For the bond-alternating structure five independent parameters (lattice constant a, bond lengths r_{C-N}, $r_{C=N}$ and r_{C-H}, angle φ of the $C-H$ bond with respect to the polymer axis) were optimized at the HF and the three correlated levels of theory as described above for the equidistant system. Here the construction of the finite model cluster is different from previous systems. As we mentioned before usually the finite model cluster is simply constructed by saturating the dangling bonds at both ends of a chain of several unit cells length by hydrogen atoms. A unit cell in the middle of such an oligomer is assumed to be virtually in the same environment as a corresponding unit cell in a polymer of infinite length, especially when only the rather short-range electron correlation effects have to be evaluated. However, in case of PMI without bond alternation such a $H[CHN]_nH$ model ($U = CHN$, $R = R' =$ H) does not have the correct symmetry, i.e., the terminal $C-H$ and $N-H$ groups strongly bias the system to yield localized π-bonds. Therefore for this system symmetric oligomers of the form $h[CHN]_nCHh$ have been applied, in which h denotes a nuclear charge of 0.5, at which a full hydrogen basis set is located. Since a symmetric oligomer has to have an odd and even number of $C-H$ groups and N atoms, respectively (or vice versa), one has to add two identical terminal groups with an odd number of electrons to come to a closed-shell model system. As it was outlined before, in the finite model cluster the convergence of $\triangle E_n$ with respect to n is much faster for the dynamical correlation energy than for the HF energy, reflecting essentially the local character of electron correlations in contrast to the long-range character of the mean-field interactions. Having at hand HF programs to account accurately for the latter effect (e.g., CRYSTAL, WANNIER) we use the finite cluster approach only for the correlation energy per unit cell. The calculations for the individual oligomers can be carried out using standard quantum chemical program packages, e.g., MOLPRO [23]. The difference in subsequent carbon-nitrogen bond lengths $\delta r = r_{C-N} - r_{C=N}$ is called the bond alternation, which is obtained by optimizing the geometry in an unbalanced way. In addition, we have also calculated the cohesive energy per unit cell at the HF and correlated level. The atomic HF-SCF, MP2, CCSD and CCSD(T) reference energies (C: -37.6769 a.u., -37.7026 a.u., -37.7148 a.u. and -37.7151 a.u.; N: -54.3821 a.u., -54.4149 a.u., -54.4188 a.u. and -54.4189 a.u.; H: -0.4982 a.u.) were obtained with

Table 4.12.: $C-N$ and $C-H$ bond lengths (Å), lattice constant a (Å), total energy E_{tot} (Hartree), cohesive energy $\triangle E_{coh}$ and polymerization energy $\triangle E_{pol}$ (eV) per CHN unit of the equidistant structure of *all-trans* polymethineimine.

Method	r_{C-N}	r_{C-H}	a	E_{tot}	$\triangle E_{coh}$	$\triangle E_{pol}$
WANNIER HF	1.314	1.099	2.261	-92.8803	8.792	0.131
CRYSTAL HF	1.313	1.099	2.260	-92.8817	8.830	0.169
MP2[a]	1.335	1.112	2.269	-93.1666	14.99	0.155
CCSD[a]	1.332	1.111	2.268	-93.1735	14.74	0.122
CCSD(T)[a]	1.337	1.114	2.270	-93.1877	15.12	0.174

[a] Correlation contributions added to CRYSTAL HF-SCF data.

the same basis sets as used in the polymer. In addition to the cohesive energy, we have also evaluated the polymerization energy and the energy difference per CHN unit with respect to the benzene analogue trimer 1,3,5-triazine $C_3N_3H_3$. The geometries of the HCN monomer and trimer were optimized at the HF-SCF, MP2, CCSD, and CCSD(T) levels employing the MOLPRO program package [23].

4.3.2. Results and Discussions

Our results for the optimized geometry, the total energy, cohesive energy, and polymerization energy per CHN unit cell of the equidistant structure of *all-trans* PMI are presented in table (4.12). The geometrical parameters obtained with the WANNIER and CRYSTAL program systems are virtually identical, whereas the total energy per CHN unit is 1.4 milli-Hartree lower for the CRYSTAL compared to the WANNIER code. One possible technical reason for this slight deviation is the use of Gaussian lobe and cartesian Gaussian functions in WANNIER and CRYSTAL, respectively. Nevertheless, the difference in the total HF energy of 1.4 milli-Hartree is still within the range of 1 milli-Hartree per atom in the unit cell, which is believed to be the accuracy of the calculations performed with the CRYSTAL program. Large quantities as the cohesive energy differ by less than 1 % (8.79 eV vs. 8.83 eV), but very small values as the polymerization energy by as much as almost 30 % (0.13 eV vs. 0.17 eV). Since the atomic and molecular calculations have been performed with cartesian Gaussian functions using the MOLPRO program package, for the other structures we refer all HF energies to the CRYSTAL HF energies. The polymerization energies refer to the fully optimized structure of the HCN monomer for each method and they are given in table (4.13).
From the table (4.12) one can see that electron correlations slightly lengthen both the $C-N$ (0.02 Å) and $C-H$ (0.01 Å) bonds as well as the lattice constant (0.01 Å). Little changes of a few hundredths of an electron volt are observed for the polymerization energy, since the number of bonds in the polymer unit cell and the monomer is

Table 4.13.: Total energy E_{tot} (Hartree) and C–N, C–H distance ($\AA$) of the monomer.

	SCF	MP2	CCSD	CCSD(T)
C–N	1.134	1.179	1.168	1.175
C–H	1.063	1.071	1.074	1.075
E_{tot}	-92.8755	-93.1609	-93.1690	-93.1813

Table 4.14.: $C-N$, $C=N$ and $C-H$ bond lengths (Å), lattice constant a (Å) as well as total energy E_{tot} (Hartree) for the bond alternating structure of *all-trans* polymethineimine. φ denotes the N=C-H bond angle and $\triangle E_{rel}$ is the relative energy (in eV) per CNH unit with respect to the equidistant structure of *all-trans* polymethineimine.

Method	r_{C-N}	$r_{C=N}$	r_{C-H}	φ	a	E_{tot}	$\triangle E_{rel}$
CRYSTAL HF	1.372	1.268	1.097	121.4	2.275	-92.8826	-0.025
HF[b]	1.362	1.262	1.094	—	2.269	—	
MP2[a]	1.376	1.304	1.112	122.4	2.287	-93.1668	-0.005
MP2[b]	1.372	1.286	1.102	—	2.281	—	
CCSD[a]	1.398	1.286	1.110	122.5	2.293	-93.1747	-0.033
CCSD(T)[a]	1.393	1.299	1.113	122.5	2.296	-93.1884	-0.019

[a] Correlation contributions added to CRYSTAL HF-SCF data.
[b] Reference [84].

the same, i.e., the triple bond of the HCN monomer is converted into two bonds of formal bond order 1.5 in the polymer. However, due to the formation of new chemical bonds significant changes induced by electron correlation are present in the cohesive energy per unit cell. The correlation contributions are 6.16 eV, 5.91 eV and 6.29 eV at the MP2, CCSD and CCSD(T) level, respectively, i.e., electron correlation accounts for 40-42% of the cohesive energy at all three levels of theory. The stability of *all-trans* PMI without bond-length alternation with respect to small oligomer ring systems was also investigated. 1,3,5-triazine $C_3N_3H_3$ is isoelectronic to benzene C_6H_6 and was calculated to be 0.469 eV per CHN unit more stable than PMI at the HF level. Again, for the isodesmic reaction from 1,3,5-triazine to PMI the correlation contributions are small: 1,3,5-triazine is 0.433 eV and 0.417 eV per CHN unit more stable than equidistant PMI at the MP2 and CCSD(T) level, respectively.
The results of corresponding calculations on the bond-alternating structure of *all-trans* PMI are listed in table (4.14). Bond alternation stabilizes PMI with respect to its equidistant form only very slightly, i.e., the energy lowerings per CHN unit are 0.024

eV (HF), 0.005 eV (MP2), 0.033 eV (CCSD) and 0.019 eV (CCSD(T)). The $C-N$ bond distances for the equidistant structures agree within 0.01 Å with the mean values of the short and long distances in the alternant case, whereas the bond alternation defined as the difference between the bond lengths of $C-N$ single and $C=N$ double bonds amounts to about 0.1 Å at all levels of theory. Due to the absence of experimental structural data we can compare our results only to other theoretical work, namely the work of Sun and Bartlett [84]. They have performed a full geometry optimization for PMI at the correlated level within MP2 theory, also using $6-31G^{**}$ basis sets. Their HF and MP2 results are basically in agreement with ours. Our value for the bond alternation is reduced from 0.104 Å at the HF level to 0.072 Å at the MP2 level, which is in satisfactory agreement with the corresponding values of 0.100 Å and 0.086 Å obtained by Sun and Bartlett. At our best level of theory, i.e., CCSD(T), we observe a 0.017 Å longer $C-N$ single bond, a 0.005 Å shorter $C=N$ double bond, essentially no change in the $C-H$ bond distance and a 0.009 Å larger lattice constant than at the MP2 level. It is noteworthy that the calculated CCSD(T) bond alternation of 0.094 Å is only 0.01 Å smaller than the original HF value. Yet unexplained is, however, why the CCSD bond alternation of 0.112 Å is even larger than the HF result, whereas it is generally believed that correlation should decrease the bond alternation. A possible reason might be that CCSD can break single, but not double bonds. The perturbative triples in CCSD(T) at least partially correct this deficiency of CCSD. On the other hand, MP2(D) will neither describe the breaking of the $C-N$ nor the $C=N$ bond and an error compensation may occur. Our results for the $C-N$ and $C=N$ bond lengths of 1.393 Å and 1.299 Å, respectively, are in modest agreement with the DFT values of Springborg [89], i.e., 1.413 Å and 1.344 Å. The deviations may be due to the fact that the latter results stem from a partially restricted geometry optimization. The agreement with the gradient-corrected DFT results of Hirata and Iwata [86], i.e., 1.373 Å and 1.300 Å, is somewhat better, although these authors applied only 3-21G basis sets. Hirata and Iwata found *cis-transoid* PMI to be about 0.16 eV per CNH unit lower in energy than the *all-trans* conformer studied so far. Del Nero and Laks [92] claimed however, that improvement of the basis sets and inclusion of electron correlation by means of DFT finally yields the *all-trans* conformer to be the most stable structure by about 0.08 eV per CNH unit. We finally note that the use of a planar structure of *all-trans* PMI was questioned by Del Nero and Laks, but their evidence was based on finite cluster calculations for the di-, tri- and tetramer $H[CHN]_nH$ $(n=2,3,4)$. Due to this open question we also investigated the *cis-transoid* and *trans-cisoid* forms of PMI at the HF, MP2 and CCSD(T) level. Our results are summarized in table (4.15). The *cis-transoid* structure was found to be 0.13 eV more stable than the bond-alternating *all-trans* conformer at the HF level, whereas no local minimum has been found at the HF level for the *trans-cisoid* case. At the MP2 level the bond-alternating *all-trans* and *trans-cisoid* forms are almost degenerate, with the *cis-transoid* PMI being 0.14 eV lower in energy. The final CCSD(T) results show the *cis-transoid* structure to be lower in energy than the bond-alternating *all-trans* conformer by 0.17 eV, whereas the *trans-cisoid* form is 0.07 eV more stable. At the

Table 4.15.: As table (4.14), but for *cis-transoid* (upper half of the table) and *trans-cisoid* (lower half of the table) polymethineimine. φ denotes the N=C-H and N-C-H bond angles, respectively.

Method	r_{C-N}	$r_{C=N}$	r_{C-H}	φ	a	E_{tot}	$\triangle E_{rel}$
CRYSTAL HF	1.374	1.277	1.080	117.7	4.004	-92.8875	-0.158
MP2[a]	1.382	1.308	1.093	118.9	3.993	-93.1718	-0.142
CCSD(T)[a]	1.362	1.336	1.096	117.0	4.065	-93.1948	-0.193
MP2[a]	1.391	1.299	1.095	115.7	4.124	-93.1675	-0.024
CCSD(T)[a]	1.393	1.312	1.097	115.6	4.125	-93.1910	-0.090

[a] Correlation contributions added to CRYSTAL HF-SCF data.

HF (MP2) level the bond alternation of *cis-transoid* PMI of 0.097Å (0.074 Å) is very similar to the one observed for the *all-trans* conformer, i.e., 0.104 Å(0.072 Å). However, at the CCSD(T) level the bond alternation of *cis-transoid* PMI is reduced to 0.026 Å, compared to 0.094 Å for the *all-trans* form.
Now we discuss the use of the incremental scheme or the simpler approach using oligomers for the evaluation of correlation energies of infinite clusters. Problems are encountered when the single-reference approach breaks down due to non-dynamical correlation effects, e.g., when studying the equidistant structure of PMI. When going from one form to the other one $C-N$ π bond is half-way broken, the other half-way formed. HF calculations for infinite systems produce a symmetric energy profile which is shown in (figure 9.) However, this is not the case for finite cluster calculations, if simply the dangling bonds of a section of n unit cells of PMI are saturated with hydrogen. Such a $H[CHN]_nH$ model cluster can describe well only one form of bond-alternating PMI and formally corresponds to a Zwitter-ion with positive and negative partial charges on the terminal C and N atoms, respectively, for the other form. The correct state with unpaired electrons on the terminal C and N atoms cannot be described at the HF level. In the subsequent correlation calculations the missing non-dynamical correlation effects are accounted for and enter the poorly convergent correlation contributions added to the HF energies evaluated for the infinite system. A model cluster much better adapted for the treatment of the equidistant structure of *all-trans* PMI is the system used for the present work, i.e., $h[CHN]_nCHh$. Here both forms of the bond alternation in *all-trans* PMI are described identically well due to the symmetry of the system and artefacts caused by nondynamical correlation are much smaller. The different convergence behavior of the MP2 correlation energies per CHN unit derived from the model clusters $H[CHN]_nH$ and $h[CHN]_nCHh$ is depicted in figure (4.10) for the equidistant structure of *all-trans* PMI. Besides the convergence of the correlation energy it is also interesting to look at the convergence of the total HF and MP2 energy per unit cell. It is shown in figure (4.11). As "correct" results we took the HF energy from the Bloch-orbital-based

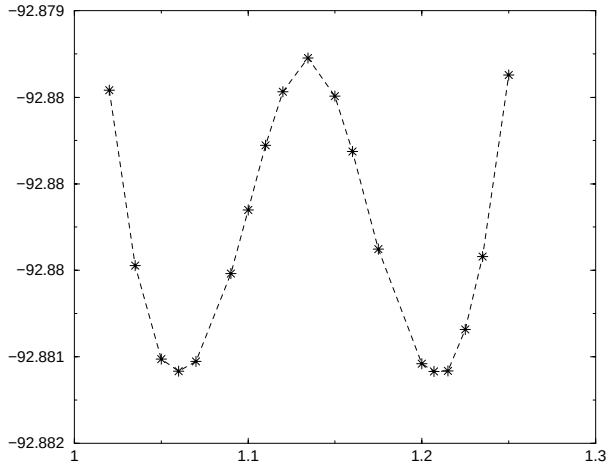

Figure 4.9.: SCF energy profile for infinite system PMI (* refer to calculated points, the dashed line being only a guide to the eye).

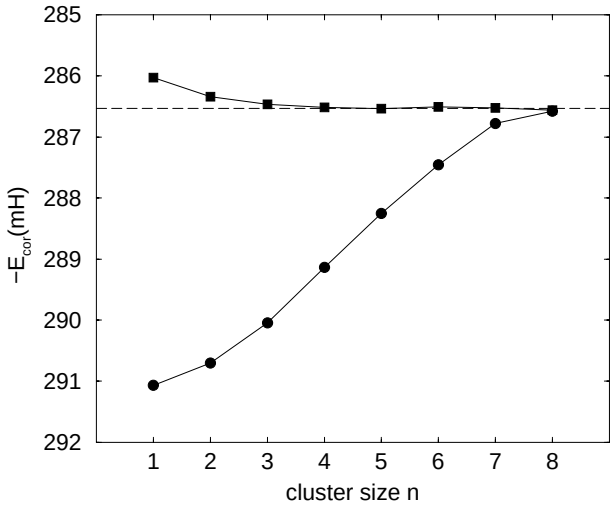

Figure 4.10.: Correlation energy per unit cell E_{cor} (milli-Hartree) for the equidistant structure of polymethineimine from MP2 calculations of model clusters $H[CHN]_nH$ (circles) and $h[CHN]_nCHh$ (squares). The cluster size n on the abszissa denotes that the energy difference of the oligomers with $n+1$ and n unit cells has been used to evaluate E_{cor}. The dashed line denotes the $h[CHN]_nCHh$ averaged values of $n = 4$, 5, 6, 7 and 8.

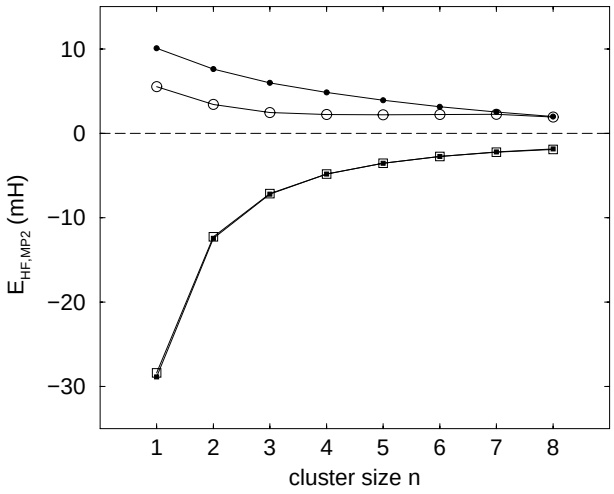

Figure 4.11.: As figure 10, but for the total Hartree-Fock (E_{HF}; filled symbols) and Møller-Plesset (E_{MP2}; empty symbols) energy per unit cell (milli-Hartree). E_{HF} is given relative to the Bloch-orbital-based Hartree-Fock result obtained with the CRYSTAL code, E_{MP2} relative to this result plus the correlation contribution from the $h[CHN]_nCHh$ oligomers from figure 10.

CRYSTAL calculations as well as this energy plus the correlation energy determined from the $h[CHN]_nCHh$ clusters (dashed zero line). In both cases the convergence towards the correct result appears to be much better for the $H[CHN]_nH$ model cluster, at least for small values of n. However, whereas the convergence behavior of the HF and MP2 energies is virtually identical for the $h[CHN]_nCHh$ clusters, in case of the $H[CHN]_nH$ systems the MP2 energy approaches the limiting value initially faster than the HF energy. We attribute the slower variation of the $H[CHN]_nH$ energies to the fact that for these clusters the π bonds are artificially localized. It is also obvious that the convergence for both clusters towards the correct result becomes tediously slow for increasing n and a milli-Hartree accuracy will be reached far beyond $n = 10$, thus making the approach impracticable for accurate total HF or MP2 energies. On the other hand, if we look at the convergence of the MP2 correlation energy per unit cell from the model cluster $H[CHN]_nH$ in dependence of the bond alternation which is shown in figure (4.12), we find out that the convergence becomes better in the region of the equilibrium structure, but still quite large values of n have to be chosen to achieve a convergence of 1 milli-Hartree or better.

4.3.3. Conclusion

A recently developed *ab initio* Wannier-function-based Hartree-Fock approach was applied to polymethineimine and yields results which are in excellent agreement with those

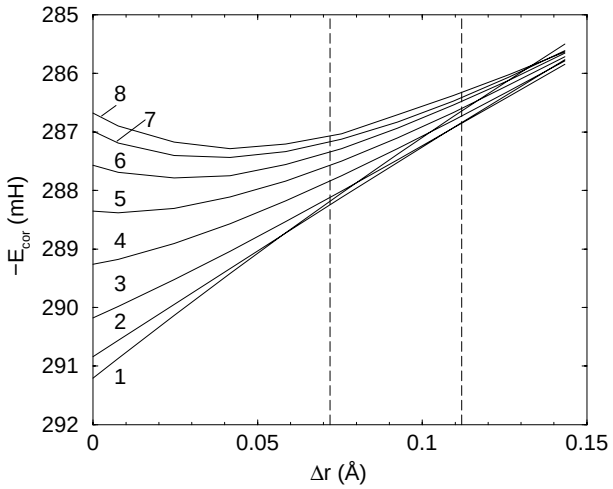

Figure 4.12.: Correlation energy per unit cell E_{cor} (milli-Hartree) of *all-trans* polymethineimine from MP2 calculations of model clusters $H[CHN]_nH$ in dependence of the bond alternation Δr (Å). The cluster size n labelling the curves denotes that the energy difference of the oligomers with $n+1$ and n unit cells has been used to evaluate E_{cor}. The dashed vertical lines denote the minimum and maximum bond alternation found in the present work.

obtained using the more common Bloch-orbital-based method. Various quantities such as the total energy per unit cell, cohesive energy, polymerization energy, and equilibrium geometry parameters were presented at the Hartree-Fock level and different levels of correlation treatment. The bond alternating structure of *all-trans* polymethineimine was found to be slightly more stable than the equidistant structure at all levels of theory. As it is the case for polyacetylene, electron correlations tend to reduce the bond alternation. In contrast to polyacetylene, the *cis-transoid* form of polymethineimine is more stable than the *all-trans* form by 0.19 eV per CNH unit. We predict $C-N$ and $C=N$ bond lengths of 1.36 Å and 1.34 Å, respectively, a $C-H$ bond length of 1.10 Å and a lattice constant of 4.07 Å. Further, the heat of polymerisation starting from 1,3,5-triazine is predicted to be 0.22 eV per CHN unit, i.e., the reaction is endothermic in agreement with experimental evidence.

5. Conclusion

In this thesis we have investigated the correlated ground state properties of polymers by applying wave-function-based *ab initio* quantum- chemical methods such as the Hartree-Fock approach, the full configuration interaction method (FCI), coupled-cluster (CC) and Møller–Plesset second–order perturbation (MP2) theory. The polymers we have studied are the boron-nitrogen polymers, i.e., polyiminoborane (PIB) and polyaminoborane (PAB), the lithium hydride chain and the beryllium hydride polymer as well as the polymethineimine (PMI). The optimized structural parameters, cohesive energies, polymerization energies, relative stabilities of isomeric forms and some band structure results are presented. The results demonstrated that quantum chemical *ab initio* methods can be applied successfully to infinite systems like polymers, although such calculations are still far from being routine.

A first step towards an *ab initio* treatment of electron correlation in infinite systems is properly treating the Hartree-Fock model. During the last years, in our group an approach was developed which allows the direct determination of Hartree-Fock Wannier orbitals within the self-consistent-field (SCF) process. The main motivation behind adopting a Wannier-function-based approach is, of course, its possible use in an *ab initio* treatment of electron correlation in infinite systems. However, being a relatively new approach, it is important to check its applicability for a variety of systems. In this thesis we have applied it to several polymers and our results have demonstrated the equivalence of this method to the standard approaches based on (delocalized) Bloch orbitals.

In the next step, having at hand the localized Wannier-type orbitals (WF), we want to include electron correlation effects by considering certain local virtual excitations from the reference wave function, keeping the rest of the infinite solid frozen at the HF level. The computational scheme to be used for this is the incremental method. Calculations based on the incremental scheme have been performed on a variety of solids. Recently, as a first step in this direction, the FCI method has been implemented with the localized Wannier orbitals for extended systems and applied in this thesis to a simple model system, i.e., the lithium hydride chain, by means of the incremental scheme.

At the present, neither the FCI method nor the incremental approach based on polymer Wannier orbitals can be used for systems with a more complicated unit cell. It still needs much more program development to come to a routine approach. Therefore, for other polymers, the electron correlation contributions to the ground state energy were calculated from finite cluster models by using a simplified scheme. We calculated the

correlation energy per unit cell at the MP2 and the coupled-cluster (CC) with singles and doubles (CCSD), including a perturbative estimate of triples (CCSD(T)) level employing the MOLPRO program.
Our results have shown that electron correlation effects in PIB and PAB contribute significantly to the cohesive energy and the band gap, but do not make any significant contribution to the structural parameters. In particular, PAB is found to be a weekly bounded covalent polymer without boron-nitrogen bond alternation. In the case of PIB, which is isoelectronic to Polyacetylene (PA), again an alternation of single and double bonds is not observed. A rapid convergence of the incremental expansion of the correlation energy is obtained for ionic systems, e.g., the lithium hydride chain model system was calculated without truncation of the infinite polymer into a finite cluster and it was demonstrated that the use of localized Wannier-type orbitals allows to compute the electron correlation effects of infinite systems. The results of beryllium hydride polymer showed that the correlation effects contributed much more to the polymerization energy than to the cohesive energy and reduced the lattice constant. In the case of PMI, the bond alternating structure was found to be slightly more stable than the equidistant structure at all levels of theory. As it is the case for PA, electron correlations tend to reduce the bond alternation. However, in contrast to PA, the *cis-transoid* form of PMI is more stable than the *all-trans* form by 0.19 eV per CNH unit. We predict $C-N$ and $C=N$ bond lengths of 1.36 Å and 1.34 Å, respectively, a $C-H$ bond length of 1.10 Å and a lattice constant of 4.07 Å. Further, the heat of polymerisation starting from 1,3,5-triazine is predicted to be 0.22 eV per CHN unit, i.e., the reaction is endothermic in agreement with experimental evidence. In all the calculations the convergency of the correlation energy with respect to the cluster size has been studied carefully by using clusters of different size within the limitations of the MOLPRO program.
Finally, regarding the use of the simplified finite cluster approach in correlation treatments of infinite systems we would like to make a short statement. Since in this approach, in order to avoid the finite size effects, the correlation energy is obtained from the difference of the correlation energies of two oligomers of n and $(n-1)$ unit cells, the success of practical calculations still depends on the appropriate termination of the dangling bonds in the clusters. Usually, the oligomers are terminated by saturating dangling bonds with hydrogen atoms, but this is not always available, e.g., for PMI. In PMI, after such a simple termination the finite model cluster does not have the correct symmetry and the situation with non-alternating bonds is not well described. Here non-dynamical became more important, i.e., partial bond breaking and forming. Special care was taken to construct an appropriate model cluster which lead to sufficiently fast convergence of the correlation contributions. The example of PMI showed that the so-called simple finite-cluster approach has to be used with some care, but it still gives quite good results when this is done. However, the advantage of this method is that it can be applied in connection with any size-extensive correlation treatment working in canonical orbitals. The disadvantage is that it becomes impracticable for large unit cells or in the 3d case. The problems can be partially overcome by interfacing highly efficient correlation codes

to Wannier-orbital-based polymer programs.

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List of Abbreviations

HF	Hartree-Fock
DFT	Density-functional Theory
LDA	Local Density Approximation
SD	Slater Determinant
CC	Coupled-Cluster
GTF	Gaussian-type basis Function
STO	Slater-type Orbital
WTO	Wannier-type Orbitals
CI	Configuration Interaction
MP2	Møller–Plesset Second–Order Perturbation Theory
FCI	Full Configuration Interaction
MBPT	Many-Body Perturbation Theory
CCSD	Coupled-Cluster Singles and Doubles
CCD	Coupled-Cluster Doubles
L-CCD	Linearized Coupled-Cluster Doubles
CCSD(T)	Coupled-Cluster with Singles and Doubles including a perturbative estimate of Triples
MSO	Molecular Spin Orbital
AO	Atomic Orbital
MO	Molecular Orbital
SCF	Self-Consistent-Field
CGTF	Cartesian Gaussian-type basis Function
DZ+P	Double-Zeta plus Polarization basis set
CISD	CI expansion with Single and Double excitations
LCAO	Linear-Combination of Atomic Orbital
LMTO	Linearized Muffin-Tin Orbital
3d	three dimensional

Atomic Units

The *Bohr radius* a_0 is defined by

$$a_0 = \frac{h^2}{(4\pi^2 me^2)}$$

Which is the atomic unit of length (*the Bohr*). In a similar way, we introduce a new atomic unit of energy, E_H, which is the Coulomb repulsion between two electrons separated by 1 Bohr:

$$E_H = \frac{e^2}{a_0}$$

This unit is termed the *Hartree*.

1 Hartree	27.2117 eV
1 Bohr	0.529177Å

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